Methane Monitoring in the European Union and Russia

Sampling in the Arctic – Zeppelin Mountain station, Svalbard (NILU)

Methane across Europe (see Workpackage 1, Figure 1.2)
Section 6.1 Background

Methane is the anthropogenic greenhouse gas that is next after carbon dioxide in importance. It presently has about half the actual warming impact (in 2002) of carbon dioxide. Europe is a major source, in landfills, gas leaks, and coal leaks, as is the Russian gas industry (Reshetnikov, 2000) that is a major EU energy supplier. Major natural sources also occur, especially in Eastern Europe and Siberia. Currently, methane is receiving much attention in the greenhouse debate (i.e. Nisbet, 2005). The bulk of atmospheric methane is anthropogenic; it can be reduced relatively quickly compared to carbon dioxide; reduction efforts are relatively inexpensive. Methane is of particular significance to poor tropical nations, as it offers the hope of real reduction in warming within decades, not centuries. It is also of much interest to those in the USA seeking a resolution of the present impasse. However, European efforts to monitor methane are very fragmented and support is insecure.

The global methane monitoring effort is traditionally heavily dependent on US, Australian and New Zealand measurements, and although much initial work had been done (Nisbet et al., 1998) there is no long-term coherent European Program at place. This, however, is a key part of the Kyoto process, and Europe is central to the emission problem. There are various excellent specific methane observation efforts in the European area, but these have mainly evolved out of University projects and the data sets do not form a coherent European programme. The very successful West European methane experiment of the mid-1990s was terminated and the partnership broken up; the multi-year EU/Russian methane programme is currently also unfunded. Isotopic studies of methane in ambient air (as opposed to source studies) are very restricted and several long-established time series are close to closure. Although concentration observations had been calibrated on the basis of USA standards, the European data sets for methane concentration were not well enough intercompared in the past. The situation is much worse for isotope measurements, and, moreover, the European data sets were not easily accessible for modelling studies. Regional modelling of methane emissions in Europe and in Russia (including Siberia) is limited by insufficient data. Global models are primarily based on the USA data set that, though it does include Atlantic/Arctic data, is primarily focussed to the USA and Pacific.

A scientifically sound, transparent and verifiable monitoring system for methane in Europe is a clear prerequisite of the Kyoto process. Such a system must include both concentration and isotopic time series, measured and inter-compared in a way that is open to modellers. The modellers in turn use the data, together with analyzed wind fields (ECMWF) to assess regional emissions by source and seasonality, and also global budgets by region, source and season. Presently, Europe does not have such a system. The MethMonitEUr project has successfully helped to improve this unsatisfactory situation and build the basis of a pan-European methane monitoring effort.
Section 6.2. Scientific/technological and socio-economic objectives

The key objective of the project was to create a basic European methane monitoring network, that is valuable in its own right, and can serve as the pilot and template for a long-term monitoring programme in Europe. The main goal was to unify European efforts to monitor methane in the Atlantic background air, in the Arctic, and over the landmass of Europe and Russia. The programme aimed at providing the basis of an integrated European methane monitoring effort.

Integration of the European measurement program includes inter-comparison with US and Australian/NZ work, to contribute to the global data set and hence serve both, as the basis for regional and global modelling studies. This allows the monitoring network to contribute to verification of compliance with Kyoto obligations. The network is based on existing long-term methane monitoring within the consortium, and, for the future aims at investigating on possible extension by adding new or existing sites.

The work was done in close linkage with existing related Carbon Dioxide measurement programmes and general Carbon Gas measurement projects. CarboEurope at present has only a small methane component. The intention of this programme was to combine efforts with CarboEurope on one hand and secondly develop close co-ordination with other GMES projects, seeking joint opportunities wherever possible and useful.

**Methane Monitoring (WP1)**

**Concentration:** Methane concentrations are monitored at a set of Atlantic, Arctic and inland stations. This includes flask, integrated, or continuous sampling, at Neumayer, Mace Head (Atlantic); Zeppelin, Pallas, Alert, Ob river (Arctic), London, Paris, Heidelberg, Krakow, St. Petersburg (Inland).

**Isotopes:** δ13C in Methane is measured to high precision in integrated or spot samples at Atlantic (Mace Head), Arctic (Alert), and Antarctic (Neumayer) stations where concentration data are collected, at a precision adequate to measure isotopic seasonality in the background atmosphere. At regional stations (Egham/London), isotope measurements are performed only episodic. These measurements were planned to be continued during the project.

**Atmospheric 222Radon Monitoring (WP2)**

Before the start of this project, 222Radon was measured at Atlantic (Mace Head) and Arctic (Alert, Zeppelin) and at two regional Inland stations (Paris and Heidelberg). These measurements were to be added at two inland sites, London, and Krakow, to allow for regional methane emissions estimates with the 222Rn-Tracer-Method (Levin et al., 1999; Biraud et al., 2000).

**Intercomparison Exercise (WP3)**

A round robin program of intercomparison between labs had to be carried out, to create a comparable European data set to serve as a basis for modelling isotopic as well as concentration data. Inter-comparison is not only necessary within European groups but also with USA and Australian/NZ labs to create an integrated global data set, for concentrations and isotopes.

**Regional (and global) Modelling (WP4)**

Concentration and isotopic methane data as well as 222Radon data will serve as the basis for regional models, that use ECMWF wind fields to assess and verify emissions from selected regions (Europe, the Arctic, Siberia). Emphasis is placed on utilizing the models to develop sampling strategies to determine regional fluxes in a quantitative way.

**Assessment of Problems in Monitoring & Synthesis (WP5)**

The programme aimed at designing and planning for a sustained European methane monitoring programme, integrated as part of the wider GMES programme under the 6th Environmental Framework Programme.
Section 6.3

Applied methodology, scientific achievements and main deliverables

Workpackage 1: Methane Monitoring Network

The purpose of the project was to unify existing methane observational programmes in Europe. Figure 1.1 shows a map with the existing measurement sites run by the partners of MethMonitEUr. Continuous concentration monitoring was performed in the Target Period of 2002-2004 at the Arctic sites Zeppelin (MISU/NILU) and Pallas (FMI), at the mountain site Kasprowy Wierch (UMM) as well as at the urban inland sites Egham/London (RHUL), Gif-sur-Yvette (LSCE), and Heidelberg (UHEI-IUP) while semi-continuous observations were made at Voeikovo and Krakow (UMM). Two-weekly or monthly integrated sampling was performed at Alert (UHEI-IUP), Voeikovo (RCRSA), St. Petersburg (RCRSA), and Krakow (UMM). Regular flask sampling was conducted at Mace Head (NUI/RHUL) and Schauinsland (UHEI-IUP) station. $\delta^{13}$C-CH$_4$ analyses were regularly made on the integrated samples collected at Alert (UHEI-IUP) and on the flask samples from Mace Head (RHUL).

In addition to the regular concentration and isotope observations, campaign work of atmospheric CH$_4$ observations was performed by RCRSA in Siberia in the Ob river area, one of the major gas exploitation areas of the world. This work was supplemented by isotopic analyses by RHUL. Also a regional survey of methane concentration measurements was carried out by UMM in the coal mining area of Upper Silesia, Poland.

Figure 1.1: Map of CH$_4$ and $\delta^{13}$C-CH$_4$ measurement sites in Europe, Siberia and the Arctic
From Figure 1.1 it is most obvious, that Southern Europe is not covered by observations, a problem that needs to be addressed in any future integrated CH₄ monitoring network for Europe. Figure 1.2 gives an overview of observed mixing ratios at the various sites. There is a clear trend of increasing mixing ratios from marine (Mace Head, Izana) towards continental mountain sites (Schauinsland, Kasprowy) with highest concentrations at the rural inland sites. Among these, in the target period of 2002-2004 Krakow shows the highest values followed by St. Petersburg and London. This is most probably caused by local emissions in the immediate vicinity of these stations. Compared to these, Voeikovo and Heidelberg mixing ratios are at the lower end.

1.1 Detailed description of results from individual monitoring stations:

**Continuous site: London (Partner 1, RHUL)**

The Royal Holloway air sampling site (51.4°N, 0.6°W), is located 32 km WSW of the City of London, on the side of Egham Hill. It is ideally located to measure near background air from the SW, or polluted air from London and continental Europe to the East. “London” is an ill-defined geographic unit. Rather than use the irregular bounds of Greater London, the London Atmospheric Emissions Inventory (Buckingham et al., 1998) used the M25 motorway as the boundary. For the purpose of London emissions estimates in the present work, the same boundary, enclosing an area of 2466 km², will be used. The laboratory / air collection site is 1.5 km outside this perimeter.

Ambient air is collected from above the roof of the Geology Dept., at about 60m ASL, 15m above local ground and 45 m above the main London basin. The site samples air that is close to local ‘Atlantic background’ from the 200-240° sector, often sampling relatively clean air from the Azores high in summer when other UK / Ireland air sampling sites (Mace Head, Shetland) do not.

Semi-continuous (half-hourly) measurements of methane (since May 1995), carbon monoxide and hydrogen (both since Sept. 1996), and near-continuous carbon dioxide (every 5 minutes since July 1999) are made. Methane is analysed by an HP 5890 GC with FID; CO by a Trace
Analytical RGD-3 instrument, and CO$_2$ by a LiCor 6252 NDIR instrument. Radon has been measured at 30 minute intervals since May 2003 as part of a collaboration with IUP-Heidelberg.

Carbon isotopes of methane have been measured to high precision (0.03‰ on replicate $\delta^{13}$C analyses) on large tank samples. The record extends from 1995, including 10 diurnal campaigns during the 1996-2000 period. Modifications have been made over the last 2 years to a GC-IRMS instrument installed in 2003. The GV Instruments Trace Gas preparation system is coupled to an IsoPrime mass spectrometer, and now achieves moderately high precision, on small samples (75mL). Precision is 0.05‰ for $\delta^{13}$C of CH$_4$, 0.03‰ for $\delta^{13}$C of CO$_2$ and 0.05‰ for $\delta^{18}$O of CO$_2$ for six consecutive analyses of an internal secondary standard tank. This means the method is capable of identifying individual local source types within the atmospheric record. Since additional automation was installed in November 2004, this now has the capability to analyse once every 17 minutes from an automated air inlet and only requires liquid nitrogen refill once every 8-hours.

Primary calibrated standards used at RHUL for the measurement of carbon gases are bought from the NOAA laboratory and recalibrated / refilled every 3-5 years. Currently the laboratory uses 3 of these and delivery of a new standard calibrated for all carbon gases and CO$_2$ isotopes is imminent. Standard calibrations are in bold, internal calibrations in plain type:

- CO$_2$ (ppm) $\text{NOAA-1 } 373.6$, $\text{NOAA-2 } 420.1$ and $\text{NOAA-3 } 372.1$
- CH$_4$ (ppb) $\text{NOAA-1 } 1811.4$, $\text{NOAA-2 } 2024.2$ and $\text{NOAA-3 } 1803.1$
- CO (ppb) $\text{NOAA-1 } 157.9$, $\text{NOAA-2 } 311.5$ and $\text{NOAA-3 } 102.0$.

Diurnal cycles are the largest events in the CO$_2$ record. CO$_2$ cycles by circa 30 ppm on many summer days and by about 5 ppm on uneventful winter days, with noticeable rush hour peaks at 08.00 and 18.00 GMT in winter (one hour earlier in summer). In major anticyclonic events the scale of the cycle is greater with CO$_2$ reaching up to 540 ppm. The CO diurnal cycle (circa 100-200 ppb on uneventful days with flowing air) broadly correlates with the CO$_2$ cycle, but regularly reaches in excess of 1000 ppb during rush-hour under anticyclonic conditions. The methane cycle (circa 100-200 ppb on uneventful days) is represented by overnight build-up under inversion conditions, with mixing ratios reaching 6000 ppb during long-lived anticyclones.

Seasonal cycling is also strong, though far less marked than diurnal change. Methane is lowest in July typically, and between 150ppb (late 1990s) to <100 ppb (presently) higher in early spring (February-April). Inter-annual changes are much smaller.

A rapid CH$_4$ decline in mean monthly concentrations of more than 10 ppb per year in the late 1990s has now given way to years in which there is little change (Fig. 1.3). Thus extracting valid annual change in London air from the noisy continuous record is subject to the caveat that the signal is much weaker than the noise. A long monitoring record is also required to remove the effects of anomalous meteorological years such as the hot summer of 2003 which is related to significantly higher carbon gas concentrations, and the longer-term impacts of the North Atlantic Oscillation. On a wider Northern hemisphere scale there are changes which can effect carbon gas concentrations in ‘background’ air arriving at the Egham site, most notably the effects of high spring and summer temperatures in Canada, resulting in high emissions of methane from wetlands and high CO and methane due to boreal forest fires.
Figure 1.3: Atmospheric methane at Egham/London. Mixing ratios decreased steadily from 1996-1999, but have shown no annual decrease since 2000.

Figure 1.4: $\delta^{13}C$ of methane in 22-L tanks samples from Mace Head and West London over a 6-years period.

Tank samples for isotopic analysis have been collected on site at Royal Holloway since 1995, concentrating on sampling the SSW-WSW background sector since 1999. There is a strong correlation between air from the ‘background sector at RHUL (Fig.1.4) and air from the Atlantic sector at Mace Head (Fig: 1.4 and below). Most $^{13}C$-enrichment is in spring time (April-June) with the biggest $^{13}C$-depletions in August. The rapid change from June to August can be related to maximum destruction of methane by reaction with OH in late June followed by maximum northern wetland emissions in August.
**Tank sampling site: Mace Head (Partners 1 & 5, RHUL & UIG)**

Mace Head Atmospheric Research Station is located in Connemara, approximately 88km east of Galway city (53° 20’ N, 9° 54’ W). It offers exposure to relatively clean westerly air masses off the Atlantic ocean (the clean sector generally considered to be from 180° through to 300°). Significant pollution events also occur at the site when European continental air masses, generally originating from an easterly direction, reach Mace Head. The site is also part of a number of other international research networks including the Advanced Global Atmospheric Gases Experiment (AGAGE) and the Climate Monitoring and Diagnostics Laboratory/National Oceanic and Atmospheric Administration (CMDL/NOAA) co-operative flask sampling network. AGAGE take high-resolution measurements of a range of atmospheric compounds including methane.

![Mace Head Atmospheric Research Station](image)

**Figure 1.5:** Left: Mace Head Atmospheric Research Station, upper laboratory. Right: Estimate of the contribution of various geographical sectors to air masses arriving at Mace Head.

Fig 1.5 shows an estimate of the contribution of various geographical sectors to air masses arriving at Mace Head. These were calculated using 120 hour back trajectory end points and categorising each trajectory into one of 8 sectors. It can be seen that more than a quarter of the air masses (29%) are not influenced during that period by any land sources. Over 60% of the air masses are westerly in origin and this is consistent with Irish climatology reports.

Tank samples were taken in bi-weekly intervals from the upper laboratory as part of the MethMonitEUr program. These samples were analysed at Royal Holloway, University of London for both methane mixing ratio and δ^{13}C. The results from the 9-year period of observations are shown in Figure 1.6. There is a strong (anti)correlation between CH₄ mixing ratios and δ^{13}C-CH₄ data throughout the record. Analysis of 2001-2003 Mace Head data highlights a CH₄ (and CO) anomaly for the last 5 months of 2002. This correlates with some ^{13}C-enrichment in Canadian trajectories and is tentatively related to intense forest fires in Quebec during August 2002. The mean isotopic ratio remained relatively constant at −47.4‰ for 1998-2001 but was followed by a growth rate of +0.1‰/yr over the next 2 years coinciding with the stabilisation of the methane mixing ratio.
Figure 1.6: $\delta^{13}$C and mixing ratio of methane in 22-L tanks samples from Mace Head over a 9-years period.

**Continuous/integrated sites: Voeikovo and St. Petersburg (Partner 1.1, RCRSA)**

Voeikovo (59°57’N, 30°42’E, 72masl) is located east of St. Petersburg, 12 km outside the administrative boundary of the city. The Voeikovo vicinities are hilly and covered by the mixed forest. In the eastern direction there is vast lowland spreading about 20 km towards the Ladozhskoye Lake coastline. The industrial zone of St. Petersburg extends in the direction range from 200 to 310 degrees. The sector from zero to 200 degrees is relatively free of the industrial activity. Monthly integrated air sampling for CH$_4$ analysis started already in 1996 in the framework of a number of INTAS-funded projects.

Summer diurnal cycles are the main contributors to the methane variability at Voeikovo. Nocturnal methane concentration growth from urban emissions usually lasts 5-10 hours and has an amplitude of the order of hundred ppb. Averaged CH$_4$ diurnal cycles for different meteorological conditions are presented in Figure 1.7.
Figure 1.7 Averaged diurnal cycles for different meteorological situations observed at Voeikovo: (1) wind speed < 3 m/s; (2) wind speed > 3 m/s; (3) temperature > 10 °C; (4) temperature < 10 °C; (5) temperature > 10 °C, wind is from urban sector (200-300°); (6) temperature > 10 °C, wind is from clean sector (0-175°).

A comparison of the averaged diurnal CH₄ cycles - depending on wind direction - for observations from 1996-2000 respectively 2003-2004 is shown in Figure 1.8. Wind direction dependence for low wind speed samples shows the influence of St. Petersburg emissions in the sector from 200 to 300 degrees. For the air masses coming from southern sectors (most probably from pollutant regions of Eastern and Western Europe) CH₄ concentration is about 40 ppb higher than for northern wind directions. This is in accordance with the results of back trajectory analyses, performed for 1996-1998 for Voeikovo by RHUL in the frame of an INTAS project. The concentration level and major features of wind direction dependence for the period of 1996-2000 and 2003-2004 are in a close agreement (Fig. 1.8). This indicates that no significant changes occurred in local and regional methane emission between the two periods. Some discrepancy is observed in the sector of wind direction from 60 to 150 degrees with a decrease of CH₄ mixing ratio at about 20-30 ppb from 1996-2000 to 2003-2004.

Figure 1.9: Averaged wind direction dependence of CH₄ concentration for the samples from data populations 1996-2000 and 2003-2004 years measurements.
Monthly integrated CH$_4$ concentrations at Voeikovo and St. Petersburg.

Monthly mean CH$_4$ mixing ratios derived from integrated samples collected at Voeikovo and St. Petersburg are shown in Figure 1.9 in comparison to concentration measurements at the Arctic coastal station Teriberka. Unfortunately, the observational series in St. Petersburg was disturbed by deployment of a steam generation unit close by the measurement site in 2003.

The CH$_4$ excess at Voeikovo over Arctic background showed a downward trend from 1996 to 1999 of $-7.8 \pm 4.4$ ppb per year, and an upward trend from 2000 to mid of 2004 of $+5.0 \pm 2.9$ ppb/yr. The mean CH$_4$ excess was $+83 \pm 33$ ppb at Voeikovo and $+170 \pm 53$ ppb at St. Petersburg. The pattern of decreasing continental methane excess observed in Voeikovo for 1996-1999 was similar to that observed in the catchment area of Heidelberg, compared to Atlantic background, where the decline rate was 9 ppb/year for the period from 1992 - 1997 (Levin et al, 1999).

![Figure 1.9: Monthly mean concentration in ambient air at Voeikovo and St. Petersburg with concentration data at the Arctic coastal station Teriberka.](image)

### Continuous site: Zeppelinfjellet (Partner 2, MISU & NILU)

The Zeppelin Station is an air-monitoring research station situated on Mt. Zeppelin (475 m.a.s.l) in Ny-Ålesund on Svalbard (N 78° 54’ E 11° 53’). Normally the site is above the planetary boundary level, thus limiting the influence of local sources of methane. The station is a background station and contributes to several networks like the CMDL cooperative Air Sampling Network (Dlugokencky et al., 1994), the Global Atmosphere Watch (GAW), the Arctic Monitoring and Assessment Programme (AMAP) and the EMEP program (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe). The continuous methane measurements were started in 1997, but from the summer 1999 to the beginning of 2000 a new station was built to replace the old one at Mt. Zeppelin.
Figure 1.10: Zeppelin station: Early sun

Ambient CH₄ measurements at Zeppelin Station are performed with a Carlo Erba FRACTOVAP 4160 gas chromatograph with a FID detector. The NOAA flask dataset together with the daily mean GC data is plotted in Figure 1.11.

Figure 1.11: Methane at Zeppelin from 1994 to 2004 in 10⁻⁹ mole/mole (ppb). Blue crosses are daily averaged GC measurements, turquoise circles are flask data taken approximately once per week. Red curve is a harmonic fitted function to the flask data, and black curve is a harmonic fitted curve to the GC measurements.

The winter peaks in methane are consistent with the climatology for Ny-Ålesund presented by Eneroth et al. (2003), coinciding with cyclonic activity and strong winds in the whole Arctic region. In connection with this, air travel along trajectories is observed that often has had its path over Russia and Siberia before arriving in Ny-Ålesund. In these regions there are strong sources of methane both from gas-fields and natural wetlands, which could be a reason for the peaks in the data at Zeppelin station. During summer the weak pressure gradients in the Arctic result in
light and variable winds, shorter trajectories and less air coming from regions with strong methane sources. Hence summer peaks in methane are not so common.

All the flask data for Zeppelin and the daily means of all data were compared and fitted with harmonic functions (Heimann et al., 1989) (compare Figure 1.11). The function fitted to the flask data (red line) showed a trend of 3.63 ppb/year while the function fitted to the daily mean data from GC measurements (black line) showed a trend of 3.34 ppb/year. The global growth rate of methane, determined using the measurements from the NOAA/ CMDL cooperative air sampling network, had since 2002 been between 1 and 5 ppb/year. The difference of the two curves fitted through the two data sets was not constant, but in the region where they overlap, it was around 20±5 ppb. We have here fitted the data to a harmonic function with constant increase rate based on the present short time-series. The constant increase rate was also used for the flask data. In reality the increase rate is not constant, but varying with time and has not been constant during the past decade, but the present time series are too short to study variations in the trend.

Continuous site: Gif-sur-Yvette (Paris) (Partner 3, LSCE/CNRS)

LSCE is monitoring semi-continuously CO₂, CH₄, N₂O, SF₆ and CO in the atmosphere at Gif-sur-Yvette, France (48°45'N; 2°10'E). This is a semi rural area about 20 km South-West of Paris. The station is mainly surrounded by agricultural areas and residential zones. Analyses of the meteorological data have shown, that during high wind speed (>5 m/s) the dominant wind direction in winter is South West and in summer South West or North West, respectively. When wind speed is lower than 5 m/s Gif station is frequently under the influence of the polluted air from Paris.

![Gif-sur-Yvette and Mace Head CH₄ and ²²²Rn mixing ratios](image)

Fig 1.12: CH₄ and ²²²Rn mixing ratios at Gif-sur-Yvette station and ²²²Rn at Mace Head.

The air inlet is located on the roof of the laboratory at about 12 m above local ground for the trace gases analysis system, and about 2 m above ground for the radon monitor (see WP2). Meteorological data (temperature, pressure, relative humidity, precipitation, wind speed and direction) are monitored at 58 m height on a tower about 500 m away from the Gif station.
Figure 1.12 shows the in situ CH$_4$ and $^{222}$Rn measurements at Gif-sur Yvette together with the $^{222}$Rn measurements at Mace Head. In general the CH$_4$ mixing ratios at Gif station varies between 1800 ppb and 2000 ppb with some pollution events of up to 2600 ppb.

The mean diurnal cycle of all species throughout the season is shown in Figure 1.13. CH$_4$ follows the same diurnal variation as the other trace gases. Maximum diurnal cycle amplitudes correspond to maximum cumulated solar irradiance reaching the surface, which yields latent and sensible heat fluxes that both promote boundary layer growth, and in contrast, episodes of stable conditions during the night. The maximum in concentration is thus reached just before sunrise at 7:00 AM UT during fall and winter, 6:00 AM UT during summer, and 5:00 AM UT during summer. For CH$_4$ we found the smallest amplitude of about 25 ppb during winter and the largest amplitude of about 60 ppb during summer.

Fig 1.13: Mean diurnal cycles observed at Gif-sur-Yvette in Winter (DJF), Spring (MAM), Summer (JJA) and Autumn (SON) for $^{222}$Rn (grey triangles), CO$_2$ (black circles), CH$_4$ (black diamonds), N$_2$O (black squares) and SF$_6$ (open circles).

**Continuous site: Heidelberg and flask sampling site Schauinsland (UHEI-IUP)**

Heidelberg (49°24'N, 8°42'E, 116 m a.s.l.) is a medium-sized city (139 000 inhabitants) located in the upper Rhine valley, about 20 km east of the industrial area Mannheim/Ludwigshafen. The local wind system in Heidelberg is dominated by alternate north/south flow along the Rhine valley, but there are also frequent easterly winds from the Neckar valley. Due to its location in a rather flat valley of approximately 40 km width and mountain hills up to 500m above the valley to the east and west, during clear nights surface inversions with high concentration pile-ups of soil-borne trace gases such as CH$_4$ are frequently observed. In contrast to local winds, large scale back-trajectories do clearly demonstrate predominance of a westerly air mass influence.

The continental GAW station Schauinsland (47°55'N, 7°55'E, 1205 m a.s.l.) is part of the atmospheric monitoring network of the German Environment Agency, Berlin (UBA). The station is situated on a mountain ridge in the Black Forest, in south-west Germany, at an elevation of about 1000 m above the highly populated Rhine valley. During night, the station is usually sampling air from above the Rhine valley inversion layer (free troposphere), while during the day, particularly in summer, due to up-slope winds the Schauinsland station frequently measures air masses influenced by local and regional CO$_2$ sources and sinks. The station is surrounded by meadows and woods; during winter the ground is largely snow covered. At Schauinsland flask samples for trace gas analysis at IUP have been collected since 1993.
The Heidelberg Institute building is located on the University campus in the outskirts of Heidelberg. From July 2000 onwards, ambient air was collected alternatively from two ventilated intake stacks located on the roof of the building at about 25m above ground at the south-west and the south-east corner of the building. At both locations, the sample air is dried cryogenically to a dew point of -40°C. Atmospheric CH₄ mixing ratios (as well as CO₂, CO, N₂O, H₂ and SF₆) are measured quasi-continuously with an automated gas chromatographic system coupled to a flame ionisation detector (FID) for CH₄ detection (and a nickel catalyst (HP5890, Hewlett Packard) for CO₂ conversion to CH₄). N₂O and SF₆ are detected with an electron capture detector (HP-ECD) while H₂ and CO are detected via reduction gas analysis (RGA-3, Trace Analytics) The routine measurement method takes half an hour and includes two standards and 1–4 ambient air injections, alternatively from the two different intake lines. In the case of automated flask analysis (i.e. Schauinsland flasks), three flask samples replace three ambient air measurements in a half hourly interval (Levin et al., 1999).

Calibrations are performed with natural-air standard gas mixtures every 15 minutes. The working gases consist of dried Heidelberg air, pressurised into high pressure cylinders using a diving compressor (Bauer). Working gases are calibrated against a suite of primary laboratory standards (purchased from NOOA/CMDL), and calibrated for CH₄ in the concentration range of 1750-1900 ppb. As a long-term stability and quality control check, a so-called “target gas” is analysed four times every 12 hours. Hourly Heidelberg CH₄ values from 2003 and 2004 are reported to the database as means of the two intake lines.

Heidelberg methane mixing ratios generally vary between about 1800 and 2100 ppb with occasionally high values up to 2500 ppb. Diurnal and synoptic variations are often correlated with ²²²Radon activities, allowing us to estimate ²²²Radon-driven CH₄ emission rates for the Heidelberg catchment area. The Schauinsland flask data generally follow the lower envelope of the Heidelberg record, indicating the continental baseline character of the site. During the last years no increasing (or decreasing) trend had been observed in CH₄ mixing ratios neither in Heidelberg nor at the Schauinsland. This is consistent with global trends.
Figure 1.14: Hourly $^{222}$Radon and CH$_4$ observations in Heidelberg 2003 – 2004. Also plotted are the CH$_4$ results from flask samples collected at Schauinsland (red circles).

**Integrated sampling: Alert, Canada (Partner 4, UHEI-IUP)**

The Global Atmosphere Watch (GAW) Background station Alert is located at 82°27’N, 62°31’W on the edge of the Lincoln Sea at the north eastern tip of Ellesmere Island in the Canadian Arctic. The station is run by the Meteorological Service of Canada (MSC) and, besides continuous CH$_4$ a huge number of other trace gases, aerosols and pollutants are monitored here. Integrated samples have been collected at Alert in large volume aluminium bags and transferred to high pressure cylinders for stable isotope analysis at UHEI-IUP. This sampling program started already in 1991, but had to be discontinued at the end of 2003 due to funding restrictions.

The measurement principle for stable isotope analyses on atmospheric methane at UHEI-IUP is based on a two-step enrichment of methane from about 500-600 litres of air on activated charcoal by a factor of approximately $1.5 \cdot 10^3$. Gas chromatographic separation of the enriched air sample from carbon and hydrogen containing gases other than methane are followed by catalytic conversion of the CH$_4$ sample on platinum to CO$_2$ and H$_2$O. The rather complex Heidelberg laboratory technique, in contrast to that used in other laboratories, also allows the D/H ratio in methane to be determined because atmospheric H$_2$ gas as well as ethane (C$_2$H$_6$) are removed quantitatively during the enrichment and gas chromatographic separation steps. CO$_2$ from the CH$_4$ combustion is directly analysed for $^{13}$C/$^{12}$C ratio by isotope ratio mass spectrometry (IRMS MAT 252, Finnigan, Bremen, Germany).
The results of CH$_4$ and $\delta^{13}$C-CH$_4$ on the Alert samples are displayed in Figure 1.15. A rather large seasonal cycle is observed in both components ($49$ ppb CH$_4$ and $0.38$‰ $\delta^{13}$C-CH$_4$) as well as a long-term trend with a total change of $\delta^{13}$C-CH$_4$ of $+0.62$ over the whole period of observations from 1991 until 2003.

**Continuous sites: Kasprowy (mountain background) and Krakow (Partner 7, UMM)**

UMM-Krakow was charged to deliver time series of methane data for two continental sites representing central-eastern Europe, ca. 2000 km from the Atlantic coast: (i) the high-altitude mountain site (Kasprowy Wierch) located in the Tatra Mountains, southern Poland; (ii) Krakow, a city of ca. 800,000 inhabitants, located ca. 100 km north of Kasprowy site.

The Kasprowy station (19°56′E, 49°14′N) is situated on the top of a mountain peak (Kasprowy Wierch) in the Tatra Mountains, southern Poland. It was anticipated that due to its exposed location (1987 m a.s.l, ca. 300 meters above the tree line) the site would, at least part time, be relatively free of local influences and may provide valuable data on the regional background levels of CH$_4$ in Eastern Europe. The mountain is situated at the intersection of three main valleys. The nearest town, Zakopane, is located in the valley, 6 km north of Kasprowy Wierch and around 900 meters below the peak. This is a small touristic town without industry. The climate at Kasprowy Wierch station is typical for a continental mountain location, with relatively large diurnal and seasonal variations of temperature, high precipitation rate, frequent changes of atmospheric pressure and strong winds. The winds are blowing predominantly along a north-south axis, with the average speed of around 7 m s$^{-1}$. Winter season with permanent snow cover begins usually in October and lasts typically for 8 months ending rapidly in June due to strong föhn circulation.

The second monitoring site is located at Krakow ca. 2 km from the city centre. Due to its location, the site experiences frequent atmospheric inversions leading to elevated levels of gaseous pollutants originating from surface emissions. With prevailing westerly circulation, Krakow is also exposed to influence of surface emissions originating in a large industrial and coal mining region (Upper Silesia), located approximately 100 km to the west of the city. Upper Silesia is an important regional source of methane released from operating mines (around 0.5 Tg of CH$_4$ in 2002).
Fig. 1.16: View of the Kasprowy Wierch monitoring station in the Tatra Mountains and the sampling site located in Krakow.

It is apparent that the near-ground atmosphere in Krakow is heavily loaded with CH$_4$ of local origin. While at Kasprowy Wierch diurnal changes of CH$_4$ mixing ratios are typically small (peak to peak amplitude of ca. 60-80 ppb, Fig. 1.17), with the broad maximum recorded during day time (advection of polluted air masses from the valley), at Krakow the amplitude of diurnal variations is ca. 10 times higher, with the maximum occurring during early morning hours.

Measurements of atmospheric $\delta^{13}$C of methane in Krakow, combined with measurements of CH$_4$ mixing ratios revealed that the local source mix is characterized by a $\delta^{13}$C value of appr. -54 %. This value almost coincides with the $\delta^{13}$C value of the gas being distributed in the city gas network (-54.4 %), and strongly suggests that the leakages of the distribution network are the primary source of methane surface emissions within the city. Indeed, usage statistics of methane gas point to losses within the distribution network in the order of 6-7 percent.

The main characteristics of CH$_4$ variability recorded at Krakow and Kasprowy Wierch stations during 2003 and 2004 are summarized in Table 1.1. It is apparent from the data that average
excess of CH$_4$ in the urban atmosphere of Krakow in 2003 and 2004 was around 200-300 ppb, with the maximum values reaching more than 3700 ppb.

Table 1.1: Variability of CH$_4$ mixing ratios at Krakow and Kasprowy Wierch stations, during the period 2003-2004.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Krakow</th>
<th>Kasprowy Wierch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum observed mixing ratio</td>
<td>3719 ppb</td>
<td>2179 ppb</td>
</tr>
<tr>
<td>Amplitude of diurnal variations</td>
<td>500-600 ppb</td>
<td>60-80 ppb</td>
</tr>
<tr>
<td>Amplitude of seasonal variations</td>
<td>150 ppb</td>
<td>30-40 ppb</td>
</tr>
<tr>
<td>Mean annual mixing ratio</td>
<td>2150 ppb</td>
<td>1850 ppb</td>
</tr>
</tbody>
</table>

Continuous site: Pallas, Finland (Partner 8, FMI)

Methane concentrations are continuously monitored at Pallas, northern Finland. In Finland anthropogenic methane emissions originate mostly from waste management, agriculture and fuel combustion. Large wetland areas in middle and northern Finland are sources of natural methane. The natural emissions from Finland are estimated to be considerably larger than anthropogenic emissions. Besides Finland, activities in neighbouring countries provide distinct features in the observed concentrations. The observations at Pallas site surrounded by wetlands in the boreal zone, some hundreds of kilometres east from Atlantic Ocean and west from Siberian gas fields, therefore, show methane signals of very variable origin depending on the air mass flow patterns.

FMI installed its GC-system (Agilent 6890N with FID and ECD detectors) for measuring methane, CO, N$_2$O and SF$_6$ at Pallas GAW station in Feb. 2004. The region is very sparsely populated (< 2 inhabitants / km$^2$).

Figure 1.18: Pallas measurement station, northern Finland.

The methane time series at Pallas station showed that during winter the episodes of high concentrations usually occurred together with elevated concentrations of other anthropogenically produced compounds such as CO$_2$ and CO. The backward trajectories showed that air masses connected to these periods had usually been transported over continental European and Russian regions. Methane concentrations decreased during spring from March until late June (Fig. 1.19), and then started to increase again as the daily temperature reached high summer season values.
and eastern and southern air flows became more frequent. Later during autumn the concentration variation was suppressed and monthly means were nudged to a second minimum in November (Table 1) before increasing again towards the late winter maximum.

![Figure 1.19: Hourly mean methane concentrations at Pallas station during February 2004 - January 2005.](image)

An example of parallel CH₄ and ²²²Radon results is shown in Figure 1.20, where back-trajectories show air mass transport from the North Atlantic Ocean in the beginning of the period and then turn to eastern Finland and western Siberia. ²²²Radon activities show increase in the air masses of continental origin and methane concentrations also show effects of a natural or anthropogenic source.

![Figure 1.20: Methane and ²²²Radon concentrations at Pallas station during August 2-4, 2004.](image)

1.2 Developments in continuous-flow stable isotopic analysis and its application on diurnal studies in Egham/London (Partner 1, RHUL)

δ¹³C analysis of atmospheric methane and carbon dioxide is a useful technique for identifying the sources and sinks of these gases and enabling verification of emissions inventories.
Continuous flow techniques can allow measurements to be made at an increased number of sites as they allow rapid analysis of small volume samples. However they are limited in their usefulness for making measurements of background air samples by the precision which can be obtained being much lower than with conventional techniques. Small modifications have been made to a GC-IRMS instrument (the GV Instruments Trace Gas coupled to an IsoPrime mass spectrometer) to improve the precision and fully-automate the inlet system. The system is being used for diurnal studies, analysing air at Royal Holloway, west of London.

**Instrumentation Development**

Conventional isotope extraction techniques as described by Lowry et al. (2001) are time consuming (up to 3 hours for collection, extraction and mass spectrometry of each sample) and require a minimum of 60 litres of air in pressurised tanks. The new system at Royal Holloway consists of a GV Instruments Trace Gas attached to an Isoprime mass spectrometer. Continuous He-flow GC-IRMS instruments, such as the Trace Gas, offer analysis of $\delta^{13}C$ using small sample volumes (75mL) and a fast analysis time (17 minutes per sample) but at an order of magnitude lower precision (0.3‰ compared to 0.03‰ for $\delta^{13}C$ of methane). A new ‘in-house’ palladinized quartz wool catalyst at 790°C has improved the average precision on $\delta^{13}CH_4$ replicates to ±0.07‰. An automated inlet system (designed in house and constructed and automated by GVI) was installed in November 2004 and now allows the Trace Gas to run continuously, only requiring liquid nitrogen addition every 8 hours. This can measure either outside air directly from an intake on the roof, or air from tanks connected to the inlet. The technique is ideal for source studies, and it is now also approaching the precision of ±0.05‰ required to identify annual variations in measurements at some background stations. This equipment is currently unique, offering small sample size, rapid analysis time, and relatively high precision on an instrument that can be quickly modified from the commercially available Trace Gas preparation system.

**Diurnal Studies in the London Area**

During high pressure anticyclonic conditions coinciding with a low wind speed, there can be a large increase in mixing ratios of methane and carbon dioxide as an inversion builds up over the London basin. The automated inlet system allows the Trace Gas to be run overnight, analysing either $\delta^{13}C$ of CH$_4$, or $\delta^{13}C$ and $\delta^{18}O$ of CO$_2$ at 30-minute intervals in air pumped down from the roof inlet. Measurements are used in conjunction with mixing ratios measured on the HP5890 gas chromatograph and the LiCor CO$_2$ analyser and wind direction data to identify the isotopic characteristics of local carbon dioxide and methane sources, e.g. landfill sites, gas boilers and vehicle emissions. Preliminary diurnal studies are being carried out for different wind directions and illustrate the range of sources in the area (Fig.1.21).
Figure 1.21. Methane Diurnal Study at Royal Holloway, 9th – 10th March 2005 (wind direction W – WNW): Time series of CH$_4$ mixing ratios and $\delta^{13}$C of CH$_4$. Measurements of $\delta^{13}$C of CH$_4$ for the secondary standard tank had a precision of 0.07‰ (1sd) in 9 analyses over 24 hours.

During the methane diurnal cycle experiment the wind direction was from the W/WNW. Methane sources in this sector are on average isotopically enriched; the main sources in that direction being gas leaks and, to a smaller extent, vehicle emissions. Methane was most enriched in $^{13}$C in the early evening, which is likely to be due to a combination of vehicle emissions and gas boilers being turned on. Further work on the isotopic characterisation of U.K. methane sources is required for better constraints on source apportionment using isotopes. Carrying out diurnal studies regularly over an extended period of time will allow seasonal and inter-annual variations in the sources of methane to be studied.

1.3 Regional survey of CH$_4$ in Upper Silesia, Poland (Partner 7, UMM)

Regional surveys of methane concentration in the near-ground atmosphere have been carried in the southern Poland in the framework of the project. South-western Poland is a relatively densely populated region, with numerous urban centres and the largest coal mining area in Europe (Upper Silesia). Coal production in this area dropped from around 200 million tons in the 1980s to approximately 100 million tons in 2002. Significant releases of methane into the atmosphere increasing local mixing ratios to more than 4000 ppb (see Figure 1.24) are associated with mining activities; the available data suggest that these releases were in the order of 1 Tg of CH$_4$ per year in the 1980s and around 0.5 Tg per year over the past few years.

Figure 1.22 shows an example of a regional survey of CH$_4$ concentrations in the near-ground atmosphere carried out on May 25, 2004, along the route starting from Krakow, passing the Upper Silesia area and ending up in another large city (Wroclaw). The survey started at 4:30 a.m. in Krakow, passing the Upper Silesia region between 5 and 6 a.m. and reaching Wroclaw at 9:30 a.m., approximately 350 km west of Krakow. Methane was measured also on the way back to Krakow which was reached at ca. 5 p.m. Methane concentrations were measured using a portable methane monitor mounted on a car. In addition, spot flask samples were collected and analysed afterwards in the laboratory. CH$_4$ mixing ratios measured on the same day at Krakow and at Kasprowy Wierch station showed values of only ca. 2200 ppb in Krakow and around 1850 ppb at Kasprowy Wierch which need to be compared with values up to 4000 ppb measured during this transect.
Figure 1.22: Regional survey of CH₄ mixing ratios (in ppm) in the near-ground atmosphere carried out on May 25, 2004, along the route starting from Krakow, passing the Upper Silesia area and ending in Wroclaw.

1.4 Siberian Field Campaigns 2003 and 2004 (Partner 1.1 & 1, RCRSA & RHUL)

Two field campaigns (2003 and 2004) were carried out in the region of major West Siberian gas fields, which is the significant source of methane of anthropogenic and natural origin. The location of measurement sites and program of observation are given in Table 1.2. Data from Korotchaevo, Novy Port, and Salim have been used for model estimations of methane emission from anthropogenic (gas fields) and natural (wetland) sources by 3D regional transport model and are presented in WP4.

Field campaign 2003.

CH₄ measurements were carried out at three sites (Korotchaevo, Salym, Novy Port) by flask sampling. Integrated technique was used to reduce possible variations of methane concentration in air. Air was pumped through gas line to plastic bag (about 10L volume) during definite time (time of integration). After filling the bag air sample was taken to vacuumed flask.

Korotchaevo.

The sampling site was located at the tower of a super deep well, 3km West of Korotchaevo settlement, 60km East of N.Urengoi city. The tower is located at a waterlogged plain (a significant part of which is covered by small lakes) with undersized forests. The similar structure of surface is kept up to the nearest N.Urengoi gas deposit. Methane content in air at Korotchaevo site can reflect natural (swamps) and industrial (gas deposits) sources influence. Air samples were taken at the territory around the tower to check presence of local sources. No significant sources were detected.

Table 1.2 Measurement sites and sampling program during the Siberian field campaigns

<table>
<thead>
<tr>
<th>Sector of gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling site, Location</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>Korotchaevo 65° 57’ N 78° 08’ E</td>
</tr>
<tr>
<td>Novy Port 67° 51’ N 72° 49’ E</td>
</tr>
<tr>
<td>Salym 60° 04’ N 71° 29’ E</td>
</tr>
</tbody>
</table>

The height of the tower is about 65m. Inlet ends of air sampling lines were located at 20m, 30m and 60m height. The sampling program is described in Table 1.2. A significant height dependence of methane concentration (200-600ppb difference between levels) was recorded on 01.09.03 under a wind direction of about 270° and wind speed of about 1m/s (see Fig.1.23). A similar situation but with smaller gradients and night-time increase was observed on the 12.09.03.

![Figure 1.23: Methane night time accumulation on 31.08-01.09.03 at Korotchaevo tower.](image)

**Novy Port.**

The sampling site was located at the weather station Novy Port (Novy Port settlement, West coast of Ob gulf). The environmental continental territory represents slightly hilly plain with significant areas of the humidified grounds, set of small lakes, small rivers and streams. The Ob gulf coast is 30m to the South and Southeast of the weather station. The nearest gas deposit (Yamurgskoe) is located at the opposite coast (Eastern) of Ob gulf, the width of the gulf at this...
place is 60-70km. Ob gulf was free of ice during campaign. Methane content in air at Novy Port (like at Korotchaevo site) can reflect natural (swamps) and industrial (gas deposits) sources influence. The inlet of the air sampling line for 30min integrated sampling was located at 5m height. Four series of integrated sampling were carried out to record night accumulation under low (<5m/sec) wind speed conditions.

Salim.

The environmental territory is covered by mixed forest with great number of small rivers and lakes. Significant areas are covered by bogs. These bogs are part of the great Vasugansko b. Powerful industrial sources are located far away from this site. So, methane content in air at Salim site can reflect mainly natural sources influence. The inlet of the air sampling line for 30min-integrated sampling was located at about 7m height on a mast, installed in the outskirts of the Salim settlement.

Field campaign 2004.

An extended measurement program was performed at Korotchaevo, which involved CH₄ measurements by GC system, chamber measurements of methane fluxes from swamps and air sampling for isotopic analysis. Intensive sampling program at station New Port was carried out.

Atmospheric CH₄ and isotopic measurements at Korotchaevo tower.

The GC system was installed close to the Korotchaevo tower. Air samples were taken from three levels of the tower (20, 30 and 60m) through plastic tubes every 20 minutes. Wind speed, wind direction, and air temperature were recorded by automated weather station.

Significant variations of methane concentrations (in the range of 1850-2600 ppb) were recorded in 2004. Height dependence of methane concentration was weak (maximum difference of concentration at different levels was about 100ppb) and sometimes was inverse (lower concentrations from low level). This kind of height dependence indicates that source of methane is remote and emitted methane well mixed during transportation.

Bag samples collected at 20, 30 and 60m heights on the tower at Korotchaevo were also analysed for δ¹³C of CH₄ at RHUL and apportioned to gas and wetland sources. Although the expected differences with height were not observed due to the meteorological conditions during September 2004 the results confirm the findings of 2 previous campaigns relating wind directions to methane sources. Tank samples of ambient air were collected overnight for δ¹³C analysis of methane during the summer (August-September) campaigns of 1999 and 2000, as part of INTAS-funded projects. The ambient air samples give a range of calculated δ¹³C source signatures from –67.3 to –49.3‰, the end members corresponding to sampling areas expected to contain only wetland or gas emissions and confirmed by back trajectory analysis for sampling times.
Table 1.3: Source signature calculations for methane in air samples collected from 60m height on the Korotchaev tower during Sept. 2004.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Background (ppb NOAA)</th>
<th>Sample (ppb NOAA)</th>
<th>δ¹³C (ä) (backgr)</th>
<th>δ¹³C (ä) (sample)</th>
<th>δ¹³C (ä) (source)</th>
<th>% gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>21/9/04 09:05</td>
<td>1807</td>
<td>2254</td>
<td>-47.42</td>
<td>-47.90</td>
<td>-49.84</td>
<td>96.9</td>
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<td>21/9/04 10:40</td>
<td>1807</td>
<td>2022</td>
<td>-47.42</td>
<td>-47.95</td>
<td>-52.43</td>
<td>82.3</td>
</tr>
<tr>
<td>21/9/04 18:25</td>
<td>1807</td>
<td>1879</td>
<td>-47.42</td>
<td>-48.18</td>
<td>-67.16</td>
<td>0</td>
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<td>1807</td>
<td>1840</td>
<td>-47.42</td>
<td>-47.74</td>
<td>-65.14</td>
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<td>-48.19</td>
<td>-67.13</td>
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<td>27/9/04 07:40</td>
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<td>2018</td>
<td>-47.42</td>
<td>-48.29</td>
<td>-55.77</td>
<td>63.5</td>
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<td>27/9/04 07:45</td>
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<td>2029</td>
<td>-47.42</td>
<td>-47.63</td>
<td>-49.30</td>
<td>100</td>
</tr>
</tbody>
</table>

Wetland chamber experiment

The closed chamber technique was used to estimate methane fluxes from local swamps. Measurements were carried out at the nearest swamp to the tower, about 2 km distance from the tower. Five different points were investigated. All points were in circle of 15m radius. The results are given in Table 1.4. Code Bn-k means that measurements were carried out at point n, and k is the measurement number at this point.

Table 1.4: Methane flux measurements by chamber method

<table>
<thead>
<tr>
<th>Point-series</th>
<th>Date</th>
<th>Start of measurements (L.T.)</th>
<th>Soil Temper. °C</th>
<th>Soil water level, cm</th>
<th>Flux mg/m²/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-1</td>
<td>15-09-04</td>
<td>11:55</td>
<td>7,2</td>
<td>0</td>
<td>4,3</td>
</tr>
<tr>
<td>B1-2</td>
<td>17-09-04</td>
<td>10:50</td>
<td>-3</td>
<td>-3</td>
<td>7,1</td>
</tr>
<tr>
<td>B2-1</td>
<td>18-09-04</td>
<td>16:35</td>
<td>6</td>
<td>15</td>
<td>3,4</td>
</tr>
<tr>
<td>B4-1</td>
<td>21-09-04</td>
<td>17:00</td>
<td>4</td>
<td>0</td>
<td>31,2</td>
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<td>B4-2</td>
<td>22-09-04</td>
<td>17:12</td>
<td>2</td>
<td>0</td>
<td>43,2</td>
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<tr>
<td>B4-4</td>
<td>26-09-04</td>
<td>13:35</td>
<td>3</td>
<td>0</td>
<td>18,8</td>
</tr>
</tbody>
</table>
Figure 1.24: Left: Results of the wetland chamber experiment on 22/9/04 for mixing ratio build-up and changing $\delta^{13}$C of methane. This experiment had the largest accumulation rate of 43.2 mg m$^{-2}$ day$^{-1}$ and emitted methane with $\delta^{13}$C of $-65.4\%$, close to the calculations based on ambient air measurements. Right: Wetland chamber during accumulation (Photo – V. Privalov)
Workpackage 2: Continuous Atmospheric $^{222}$Radon Monitoring

Within the framework of the MethMonitEUr project, the $^{222}$Radon monitoring capability at European monitoring sites has been improved. $^{222}$Radon daughter measurements had already been routinely performed before the start of the project at Mace Head observatory since 1996, at Pallas station since 1995, at Gif-sur-Yvette since 2002, at Zeppelin since 1998, and at Heidelberg since 1994. UHEI-IUP has built two additional $^{222}$Radon monitor systems to be installed and run in parallel to CH$_4$ mixing ratio observations at Egham/London and at Krakow, Poland. Continuous $^{222}$Radon daughter observations are now available for Egham/London since May 2003 and for Krakow since June 2004. Hourly data from all sites are reported to the MethMonitEUr data base for the years 2002 – 2004.

2.1 Measurement techniques for $^{222}$Radon observations:

At Mace Head and Gif-sur-Yvette, $^{222}$Radon is measured with the active deposit method: Ambient air is pumped through a paper filter at a flow rate of about 7 m$^3$ h$^{-1}$ for 2 hours, accumulating aerosol particles on the filter. After the sampling period, the filter is placed under an alpha spectrometer (scintillator and photomultiplier), in order to measure the radioactive decay of the accumulated Radon daughters for 2 hours. The detection limit is 0.3 mBq m$^{-3}$, equivalent to 200 $^{222}$Rn gas atoms per cubic meter of air. The statistical error on the measurement is inversely proportional to the square of the number of disintegrations recorded. Thus for a 2-hour measurement period, and for a concentration of about 1mBq m$^{-3}$, the statistical error is close to 10%.

The FMI radon system is also based on measuring the activity of short-lived $^{222}$Rn progeny. The inlet of the sampling line for the radon instrument is located 6m above the ground. Aerosol is collected continuously onto a filter and counts from beta-activity on it are measured with a Geiger-Müller counter. Counts from beta counter are converted to activity concentration by taking into account flow rate and counting efficiency and assuming that the activity on the filter is from short-lived radon daughters, radon is in equilibrium with the daughters and that no artificial activity is present. Radon measurements at Pallas started in 1997 and they are recorded as hourly means (Paatero et al., 1998).

Figure 2.1: Left: Schematics of the Heidelberg $^{222}$Radon Monitor. Right: Typical $\alpha$-spectrum of the $^{222}$Rn and $^{220}$Rn daughters collected in Heidelberg on a quartz glass filter with an integration
time of one hour. The different isotopes and the thresholds for evaluation of the spectrum are also marked in the diagram (from Levin et al., 2002).

Figure 2.1 (left) shows the schematics of the Heidelberg $^{222}$Rn Monitor which is now also running at Zeppelin, Egham/London and Krakow. At a flow rate of about 0.5-1.5 m$^3$ h$^{-1}$, ambient air is continuously pumped through a quartz fibre filter (Whatman QMA, $\varnothing$ 47 mm), the flow rate is monitored with a flow meter (EL-FLOW F112AC-HAD-22-V). The $^{222}$Rn (and $^{220}$Rn) daughters $^{218}$Po ($\alpha_E = 6.0$ MeV) and $^{214}$Po ($\alpha_E = 7.7$ MeV) collected on the filter are measured in situ with a surface barrier detector (Canberra CAM AB 900 mm$^2$ active surface, energy resolution: 50 keV at an $\alpha$-energy of 5.486 MeV). A pre-amplifier converts the detector pulses into amplified voltage signals which can then be transmitted via cable over distances of up to 100 m. This allows physical separation of the filter head from the main electronic board, and thus relatively short tubing connections between filter holder and ambient air. The signal is further amplified and processed by dedicated analogue and digital electronics.

A typical $\alpha$-spectrum of the $^{222}$Rn and $^{220}$Rn daughters collected on the quartz filter within a one hour integration time is shown in Figure 2.1 (right). Due to various absorption mechanisms, the $\alpha$-spectrum is distorted to lower energies (low energy tailing). Three maxima are clearly to distinguish in the spectrum, representing the $\alpha$-activity of $^{212}$Po, $^{214}$Po and a mixture of $^{218}$Po and $^{212}$Bi. Depending on the time of the day and the degree of the filter loading, the ratio between the $^{212}$Po ($^{220}$Rn daughter) and $^{214}$Po ($^{222}$Rn daughter) may vary by nearly one order of magnitude. However, the $^{220}$Rn-derived $^{212}$Po peak can be easily resolved, and, hence, separated from the $^{214}$Po peak, allowing for an accurate determination of the $^{222}$Rn daughter activity on the filter. In order to calculate the ambient $^{222}$Rn activity from the $^{214}$Po activity on the filter, an evaluation algorithm has been developed which is described in detail by Levin et al. (2002). Depending on the measurement height above ground, the disequilibrium between atmospheric $^{222}$Rn activity and its measured $^{214}$Po daughter activity needs to be estimated. In the case of the Heidelberg, the Egham/London and the Krakow measurement sites which collect the air between 20 and 30 m above ground, a mean disequilibrium factor of 1.367 is applied as experimentally determined for Heidelberg in a study by Cuntz (2001).

2.2 Results

The atmospheric background $^{222}$Rn activity at a particular station depends on its distance from the ocean respectively on the mean residence time of the measured air over the continent. If the measurement site is located in the boundary layer, the local $^{222}$Rn activity also strongly depends on the dynamics of the boundary layer height (e.g. day/night) and on the local $^{222}$Rn exhalation rate from the soil. Similar to $^{222}$Rn, the mixing ratios of other trace substances such as CH$_4$ with sources at or close to the ground, besides their regional emission rate, also depend on the boundary layer dynamics. In the case that the $^{222}$Rn exhalation rate from the soil is known in the respective catchment area of a particular measurement site, $^{222}$Rn measurements conducted in parallel to other trace gas observations can be used to estimate the night time fluxes of the trace gas (in our case of CH$_4$) (Levin et al., 1999; Schmidt et al., 2001).

The frequency distribution of $^{222}$Rn at the continental MethMonitEUr sites for the second half year of 2004 is shown in Figure 2.2. There is a clear trend towards higher $^{222}$Rn activities with more continental character of the station: From Egham/London, Gif-sur-Yvette, and Heidelberg towards Krakow, median activities increase by about a factor of 5. The Pallas station cannot directly be compared with the other sites as it is located on a mountain top, and not in the boundary layer. Table 2.1 summarises the $^{222}$Rn characteristics for all 7 MethMonitEUr sites (also including the coastal site Mace Head and the marine site Zeppelin). The 10% percentile can be used as an indication of the “background” (free troposphere) mixing ratio while the difference between the 90% percentile and the 10% percentile can be used as a rough measure of the mean
The latter regional signal is driven by the mean regional boundary layer dynamics and by the soil exhalation rate.

Figure 2.2: Frequency distribution of $^{222}$Radon activities at the continental MethMonitEUr sites for July to December 2004. The numbers behind the station names are the median activities.
Table 2.1: $^{222}$Radon characteristics for July to December 2004 of the MethMoniTEUr sites

<table>
<thead>
<tr>
<th>Station</th>
<th>Median $^{222}$Rn mixing ratio [Bq m$^{-3}$]</th>
<th>10% percentile [Bq m$^{-3}$]</th>
<th>90% percentile [Bq m$^{-3}$]</th>
<th>Amplitude [Bq m$^{-3}$]</th>
<th>Ampl./10% percentile [Bq m$^{-3}$]</th>
<th>$^{222}$Rn soil exhalation [Bq m$^{-2}$ h$^{-1}$]</th>
<th>CH$_4$/$^{222}$Rn median all 2004 [ppb/(Bq m$^{-3}$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeppelin</td>
<td>0.15</td>
<td>0.06</td>
<td>0.45</td>
<td>0.4</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mace Head</td>
<td>0.20</td>
<td>0.07</td>
<td>1.01</td>
<td>0.9</td>
<td>(12.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pallas</td>
<td>0.90</td>
<td>0.20</td>
<td>2.00</td>
<td>1.8</td>
<td>9.0</td>
<td>21</td>
<td>10.8</td>
</tr>
<tr>
<td>Egham/London</td>
<td>1.10</td>
<td>0.39</td>
<td>3.91</td>
<td>3.5</td>
<td>9.0</td>
<td>63 (28.6)</td>
<td>100.4</td>
</tr>
<tr>
<td>Gif-sur-Yvette</td>
<td>2.24</td>
<td>0.68</td>
<td>5.55</td>
<td>4.9</td>
<td>7.1</td>
<td>35</td>
<td>20.2</td>
</tr>
<tr>
<td>Heidelberg</td>
<td>4.11</td>
<td>1.53</td>
<td>9.53</td>
<td>8.0</td>
<td>5.2</td>
<td>63</td>
<td>14.2</td>
</tr>
<tr>
<td>Krakow</td>
<td>5.47</td>
<td>2.09</td>
<td>16.31</td>
<td>14.2</td>
<td>6.8</td>
<td>34</td>
<td>29.4</td>
</tr>
</tbody>
</table>

For the 4 “continental” boundary layer sites the mean (diurnal) amplitude (90% - 10% percentile) increases by about a factor of 4 from Egham to Krakow, similar to the median $^{222}$Radon activity and the 10% percentile ($\approx$ continental background). Therefore, the ratio between individual amplitude and 10% percentile is a rather robust number throughout these sites. Obviously, the mean diurnal $^{222}$Radon amplitude at a particular site is not only depending on the local $^{222}$Radon exhalation rate (which, if derived from soil texture classes in the 2° x 2° region south-west of the stations, and using mean $^{222}$Radon exhalation rates of soil texture classes TK1: 27 Bq m$^{-2}$ h$^{-1}$; TK2: 43 Bq m$^{-2}$ h$^{-1}$, TK3: 87 Bq m$^{-2}$ h$^{-1}$, TK4: 41 Bq m$^{-2}$ h$^{-1}$; TK5: 57 Bq m$^{-2}$ h$^{-1}$; TK6: 77 Bq m$^{-2}$ h$^{-1}$ from Jutzi (2001), calculated in Table 2.1 for the sites, would vary by only a factor of two) but also from the frequency of night time inversion situations. In the case of the Egham/London site, the simply soil-texture-derived $^{222}$Radon exhalation rate is larger by a factor of two if compared to direct observations in the region (number in brackets), most probably due to the rather high soil humidity in the Egham/London area. This must be taken into account when comparing Egham diurnal amplitudes with those at Gif-sur-Yvette, Heidelberg and Krakow.
Figure 2.3: Methane-to-$^{222}$Radon ratios calculated from night-time data at the individual sites. Daily mean ratios are included in the figure and the median values (also in Table 2.1) only if the correlation coefficient for individual nights was larger than $R = 0.7$. The numbers behind the station names are the median values for all daily ratios available in the year 2004.

Figure 2.3 shows the night-time CH$_4$/222Rn ratios for the 5 continental sites for the period of individually available observations from 2002 to 2004. The ratios, if multiplied by the mean $^{222}$Radon exhalation rate from the soil in the individual catchment areas of the sites, can be used to estimate the Radon-derived CH$_4$ flux (Levin et al., 1999). While the ratios and their variability are comparable at Gif, Heidelberg and Krakow, they are considerably larger for Egham/London. One reason for the high ratios surely is the smaller soil exhalation rate at Egham/London compared to the other three sites. However, even if taking this into account would leave the “normalised” Egham/London ratios higher by a factor of three to four compared to Krakow, Gif and Heidelberg. These higher ratios are most probably due to higher CH$_4$ emission rates in the catchment area of Egham/London compared to the other stations.

This preliminary assessment of parallel CH$_4$ and $^{222}$Radon observations clearly shows that semi-quantitative estimates of trace gas fluxes (here of CH$_4$) can be obtained. However, for a reliable quantitative estimate of trace gas fluxes, using the Radon-Tracer method, more detailed information about the soil exhalation rate of $^{222}$Radon in the catchment areas of the sites would be required.
Workpackage 3: Intercomparison and Database

Data can only be used together if the yardsticks are the same. All methane measurements in Meth-MonitEUr are measured against the same set of standards, the NOAA standards, but one-way standardisation is not enough. There will always be small systematic differences. Therefore, it is necessary to intercompare between stations and laboratories by ‘round robin’ experiments, in which air samples are sent around the whole group. Each lab will differ slightly from the next, but with luck these differences can be quantified and corrected for when the data shall be used in modelling studies. This workpackage was designed to provide such intercomparisons. In addition, at a number of sites, measurements from two different laboratories exist (for example continuous observations by the national labs and flask sampling by a foreign lab or NOAA/CMDL). Comparison of these results has been assessed.

A second aim of this work package was to develop a database including all results derived from this project.

3.1 Intercomparisons

The round-robin exercise for CH₄ mixing ratios started in 2003, and has been continued in 2004. In addition, in 2004, an intercomparison (ICP) for the ^13C isotope of CH₄ has been realized. All ICP material has been provided by UHEI-IUP. For concentration intercomparison a set of three 10 litre aluminium tanks filled in Heidelberg with real atmospheric air using a breathing compressor (Purus/Utilus 10, Bauer, Germany) was used. The mixing ratios of the tanks were between 1770 and 1930 ppb CH₄. For isotope intercomparison, the following material has been added in 2004: 1 x 27 liter tank (NewZ1) of natural air ; 1 x 40 liter tank (EG96A D Int) of CH₄ in synthetic air, and 3 glass ampoules of 300ml with pure CO₂ gas.

![Figure 3.1: Difference between the mean CH₄ mixing ratios determined in individual labs from the median determined at UHEI-IUP in 2003, 2004 and 2005 for the three tanks. The coloured area shows the ±2 ppb target value recommended by the World Meteorological Organization.](image)

Details of the measurement procedures in the different laboratories and reference materials used are given in Appendix 1. All European laboratories participated in the two circulations of the ICP tanks for mixing ratios. The results of this intercomparison are shown in Figure 3.1. With two exceptions for the high mixing ratio at 1930 ppb, all laboratory results agree within the WMO target. In the case of the in situ flask intercomparisons, significant offsets have been observed which are summarised in Table 3.1 and displayed in detail in Appendix 1.
In the intercomparison for stable isotope ratios on pure CO2 samples (mass spectrometer comparisons) and whole air samples (CH4 extraction lines and mass spectrometer), only a subset of laboratories participated, including two labs in the US and New Zealand. The results for the pure CO2 standards for $\delta^{13}C$ and $\delta^{18}O$ in CO2 are displayed in Figure 3.2. $\delta^{13}C$ results are displayed in Table 3.2 while those for $\delta^{18}O$ are given in Appendix 1.

The data show very good agreement for Pflanzenstandard for all laboratories which has intermediate values for both $\delta^{13}C_{V-PDB}$ and $\delta^{18}O_{V-PDB-CO2}$, but show greater spread toward heavier and lighter values. As this is, within analytical error, a systematic relationship for each laboratory, it is likely that this is due to behaviour and calibration of the mass spectrometer being used rather than problems of analytical procedure on individual gases. The London and NIWA laboratories show $^{13}C$ enrichment relative to the mean at light values of $-50\%$, but $^{13}C$ depletion at heavy values of $-4\%$. The opposite trend is seen for Krakow and Heidelberg. With the exception of the London and Krakow values for the Reinststandard at $-50.4\%$, all reported values are within $\pm 0.04\%$ of the mean. This suggests that further calibrations are needed at the lower end of the $\delta^{13}C_{V-PDB}$ scale, either using RM 8563 light standard at $-41.56\%$ or a light carbonate standard such as IAEA CO-9 barium carbonate at $-47.3\%$ or LSVEC lithium carbonate at $-46.5\%$. For $\delta^{18}O_{V-PDB-CO2}$ the Heidelberg, Krakow and London results are within $\pm 0.04\%$ for all 3 gases. NIWA was not included in the mean calculation due to a marked offset in values compared to the other 3 laboratories, particularly at the light end of the scale (Fig. 3.2).

### Table 3.1: Mean differences and standard deviations of mixing ratios from individual sites

<table>
<thead>
<tr>
<th>Station</th>
<th>Institutes compared</th>
<th>Mean±1σ [ppb]</th>
<th>No. of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mace Head</td>
<td>LSCE (flasks) – AGAGE (cont.)</td>
<td>-19.5 ± 5.7</td>
<td>31</td>
</tr>
<tr>
<td>Mace Head</td>
<td>LSCE (flasks) - NOAA/CMDL (flasks)</td>
<td>0.6 ± 1.6</td>
<td>17</td>
</tr>
<tr>
<td>Pallas</td>
<td>FMI (cont.) – NOAA/CMDL (flasks)</td>
<td>-1.1 ± 3.1</td>
<td>31</td>
</tr>
<tr>
<td>Zeppelin</td>
<td>NILU (cont.) – NOAA/CMDL (flasks)</td>
<td>12.8 ± 8.8</td>
<td>76</td>
</tr>
</tbody>
</table>

### Table 3.2: Corrected $\delta^{13}C_{V-PDB}$ results: intercomparison of pure CO2 gases provided by UHEI-IUP

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Corrected $\delta^{13}C_{V-PDB}$ (%)</th>
<th>Offset from Mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reinststandard</td>
<td>Pflanzenstandard (B)</td>
</tr>
<tr>
<td>UHEI-IUP</td>
<td>-50.42±0.01</td>
<td>-24.99±0.01</td>
</tr>
<tr>
<td>UMM-Krak</td>
<td>-50.50±0.01 (12)</td>
<td>-25.03±0.01 (12)</td>
</tr>
<tr>
<td>RHU-Lond</td>
<td>-50.33±0.01 (3)</td>
<td>-24.99±0.02 (3)</td>
</tr>
<tr>
<td>NIWA-NZ</td>
<td>-50.37±0.01</td>
<td>-24.98±0.01</td>
</tr>
</tbody>
</table>

Mean $\delta^{13}C$ for Pure CO2 Standard Intercomparison: 50.41 (4)
Median $\delta^{13}C$ for Pure CO2 Standard Intercomparison: -50.40

Mean $\delta^{18}O$ for Pure CO2 Standard Intercomparison: 25.00 (4)
Median $\delta^{18}O$ for Pure CO2 Standard Intercomparison: -4.42
Figure 3.2: Offset from the mean value for all laboratories reporting data for the pure CO₂ gases. Offset of $\delta^{13}_{\text{CV-PDB}}$ at left and $\delta^{18}_{\text{V-PDB-CO2}}$ at right.

The results of the CH₄ isotope intercomparison are shown in Figure 3.3 and Table 3.3. The means and 1SD’s for $\delta^{13}_{\text{CV-PDB}}$ after laboratory calibration are: NZ-1 $-47.15 \pm 0.08\%$ (5), EG 96ADInt $-50.27 \pm 0.18\%$. These precisions are not satisfactory, but may in part be due to difficulties in calibrating online continuous flow systems, which are set up specifically to analyse CH₄ and CO₂ in ambient air samples. Looking separately at the analysis by dual inlet compared to analysis by continuous flow shows that the latter are enriched by between 0.14 and 0.26%. The dual inlet means are $-47.21 \pm 0.03\%$ (3) and $-50.40 \pm 0.04\%$ (2). The constant offset between the continuous and dual inlet methods of the London group suggest that this is related to calibration and that the former need to be corrected by a further 0.1%.

Clearly, the intercomparison would have benefited from the participation of the other laboratories. While our mass spectrometer calibrations allow us to be reasonably confident about the accuracy of the mass spectrometers, the limited number of CH₄ isotope intercomparisons so far suggest that we cannot be confident of the precision produced by our preparation techniques to within 0.1%. The indication from this and previous intercalibrations is that the large sample extraction / dual inlet systems of NIWA, Heidelberg and London produce methane isotope data accurate to within ±0.05%.
Table 3.3: Intercomparison between laboratories of the $\delta^{13}C$ of methane in 2 air cylinders, by conversion to CO$_2$.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Corrected $\delta^{13}C_{\text{V-PDB}}$ (%o)</th>
<th>Offset from Mean (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EG 96AD Int</td>
<td>NZ-1</td>
</tr>
<tr>
<td>IUP-Heid</td>
<td>-50.33 (2)</td>
<td>-47.26±0.04 (3)</td>
</tr>
<tr>
<td>RHUL (DI)</td>
<td>-50.44±0.01 (2)</td>
<td>-47.19±0.01 (2)</td>
</tr>
<tr>
<td>RHUL (CF)</td>
<td>-50.32±0.09 (7)</td>
<td>-47.08±0.13 (6)</td>
</tr>
<tr>
<td>NOAA-US</td>
<td>-49.96±0.18 (24)</td>
<td>-47.05±0.06 (24)</td>
</tr>
<tr>
<td>NIWA-NZ</td>
<td>-47.19±0.02</td>
<td>-0.04</td>
</tr>
<tr>
<td>Mean</td>
<td>-50.26 (4)</td>
<td>-47.15 (5)</td>
</tr>
<tr>
<td>1 SD</td>
<td>0.18</td>
<td>0.08</td>
</tr>
<tr>
<td>Median</td>
<td>-50.33</td>
<td>-47.19</td>
</tr>
<tr>
<td>Dual Inlet</td>
<td>-50.39 (2)</td>
<td>-47.21 (3)</td>
</tr>
<tr>
<td>1 SD</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Con Flow</td>
<td>-50.14 (2)</td>
<td>-47.07 (2)</td>
</tr>
<tr>
<td>1 SD</td>
<td>0.18</td>
<td>0.02</td>
</tr>
</tbody>
</table>

As continuous flow is the likely future of atmospheric methane isotope measurement it is essential that systems are better intercompared. It is recommended that additional isotopic intercomparison exercises are included as an integral part of future European methane proposals involving isotopes and that NIWA and NOAA are included in these plans from the outset.

Figure 3.3: Offset from mean of the results of the intercomparison of $\delta^{13}C_{\text{V-PDB}}$ of methane in air samples.
3.2 Database

A database for atmospheric measurements has been established (http://www.lsce.cnrs-gif.fr/CE-atmosphere/methmoniteur). Both, continuous and flask measurements are present together with meteorological data when available. Access to the actual data are restricted to MethMonitEUR participants. A common data format is used and available on the database web page. Quality control information on the data is present in two places in each data file:

First a version number is present in the header file. It provides an indication of the processing level of the data contained in the file (for more details, see the data format document available on the database web page). Second a three-character flag is present in the data file itself as an extra column for each individual line of datum measurement. The first character is a basic quality flag indicating whether the record is to be rejected (because of instrument problems for example) or kept. The second character is a representativeness flag specifying whether the datum is more representative of local, regional or background conditions. This analysis is usually done by considering the meteorological information recorded at the measurement site. Finally the character in the third column is the comment flag.

Metadata information is also present on the web page, providing information on the dataset itself, the measurement site, data manipulation performed, the equipment and calibration used to do the measurement and contact information on the person contributing the data.
Workpackage 4 Regional Modelling

The modelling within MethMonitEUr has been performed at several levels of resolution. Trajectory studies, smaller scale case studies, regional models and global models. Particular attention has been given to regional studies but the whole hierarchy of models has been necessary to span the scales with larger scale models providing boundary conditions for the finer resolution models.

4.1 European regional modelling (Partner 2, MISU & NILU)

A 3-dimensional regional transport model MATCH (Multiple-scale Atmospheric Transport and Chemistry modelling system), 1°x1° horizontal resolution (Robertson et al., 1999) has been extensively used for statistical studies of representativeness and sampling strategies. MATCH is a Eulerian three-dimensional atmospheric diffusion model. Input of meteorological data is performed every six hour. Hourly winds are linear interpolated between the input data. The MATCH model has been developed as a flexible, offline, chemistry/transport/deposition model for atmospheric pollutants. It is used in a range of applications from urban scale studies on 1km or higher horizontal resolutions to continental scale studies on acid deposition and photochemistry. The model ranges in the vertical from surface up to the upper part of troposphere around 10 hPa divided in 31 levels. The model reads in modules of parameterisations of emissions, vertical distributions, depositions processes and chemical components. Meteorological fields (e.g. wind, temperature and pressure) from the European Centre for Medium range Weather Forecasts (ECMWF) have been extracted every 6 hours. Emission and boundary conditions were acquired from a global tracer transport model (see below). The base case described in the following variability discussion is a detailed study of one year (1998).

Snapshots from MATCH simulation of methane dispersion from Europe (Figure 4.1) during a period in April 1998 that illustrates some important aspects of how regional emissions only intermittently influence data at some monitoring stations whereas others are influenced more extensively. The sources are mainly concentrated to industrial activities in this April month and we see a distinct (red) plume emanating mainly from European (including western Russia) emissions.

The period begins with a very clear cyclone over Russia that pulls up polluted European air and pushes a wave of Arctic air (blue low concentration hook most clearly seen April 3 at 12UTC) down over Russia and Siberia. As the cyclone dissipates during April 4 it sheds an “island” of high concentration air around the Ob river estuary. There are two more similar cyclonic episodes in this period that clearly show up with blue hook shapes propagating April 9-11 and April 16 (somewhat weaker). The cold fronts have marked lower concentrations caused by cold front subsidence bringing down air from the upper troposphere.

The Mace Head site is influenced by plumes from Europe in the beginning (April 3 – April 8 00UTC) but is then clearly in Atlantic air until April 16 12UTC when a plume arrives again which is then blown back towards Europe already by April 18 00UTC. The developments over the Scandinavian Peninsula during this time slice period illustrates that there is a variable concentration situation for a station at the edge of the continent (e.g. Pallas in northern Finland). Northern Scandinavia is dominated by Atlantic and Arctic air in the beginning of the simulated period.
Figure 4.1: Snapshots of simulated time development of methane concentration at the surface level in the MATCH model. The dates and times are given for each frame. The colours indicate concentration as defined by the colour scales. Transport events that illustrate the challenges to be met by a permanent sampling network are described in text.
From April 14 and forwards there is, however, a diffuse but clear influx of European air also towards northern Scandinavia. Southern Scandinavia begins the period under Atlantic air but already on April 4 the European plume covers Denmark and the southern areas of Norway and Sweden and remains there throughout the remainder of this time-slice. Inspecting the entire period one can glean that the average concentration gradient from northern to southern Scandinavia will be robust with higher concentrations towards the south despite the high variability caused by the synoptic weather variability.

During this period the Zeppelin station on Svalbard is not influenced by European air. Some secondary effects are seen when some enhanced concentrations are advected in (April 9-10) from concentrations that at least in part emanate from the previously described cyclone-shed polluted air islands over the eastern Arctic. To make quantitative source estimates from such “secondary” plumes requires detailed meteorological information about mixing and transport in frontal zones at a level that meteorological models are probably are unable to provide.

Synoptic time-scale variations make monitoring records highly variable. Single station observational records have limited applications and the need for a network is obvious. But a network that can resolve the full intricacy of the concentration plumes must be dense enough in space and time that the shapes and temporal development can be resolved. Inspection of Figure 4.2 gives scales for such a network that are unrealistic fine to achieve without new technology or immense funding. On the regional scale there is, however, an opening in that averaging over periods longer than the typical synoptic scale and shorter than seasons (months arbitrarily chosen here) can give some robust features (as already mentioned in the discussion of the Scandinavian gradient). Figure 4.2 shows the average concentration fields for the twelve months for our base case. Stations should be placed to capture the major elements of these fields with locations in the extremes and in areas of strong gradients. There are seasonal shifts in the gradients and positioning of extremes (caused both by seasonal shifts in meteorology and in source distribution) that indicates a need for several interior stations to capture such variations. Interannual variability is not yet explored with the full regional simulation but expected (as seen in the trajectory study described below for one of the stations). This introduces a further demand for redundancy in a network to ensure that shifts in the interior are never based on a single station data record but confirmed regionally such that what really is a redistribution of methane to/from unsampled regions is not misinterpreted as a shift in sources or sinks. We can thus use the atmosphere as integrator over some weeks to give regional fluxes based on robust gradients. There are, however, seasonal changes in methane sources and sinks too. When sources/sinks change significantly on time-scales shorter than the averaging times necessary to acquire the regional gradients there will be difficulties with interpretation without high spatial resolution data.

Inter-annual variability is studied with the three-dimensional trajectory model of McGrath (1989). It is used to calculate 5-day back-trajectories for the 4-year period 2000-2003. In the model, wind fields from the European Centre for Medium range Weather Forecasts (ECMWF) are used with a horizontal resolution of $1^\circ \times 1^\circ$ and temporal resolution of 6 h. Trajectories arriving at Ny-Ålesund twice a day (00 and 12 UTC) are calculated for the pressure levels 750, 850 and 950 hPa. The total number of trajectories for the whole period is 2860, at each pressure level. They are classified into transport patterns through the use of cluster analysis. Cluster analysis is a variety of multivariate statistical analysis technique designed to explore structure within a dataset and divide the dataset into groups or “clusters” of similar cases. This initial study was made for the Zeppelin station (Pedersen and Holmén, 2005).
Figure 4.2: Monthly mean concentrations in the model domain of the base case.
Marked seasonal variations in frequency of occurrence of different clusters are seen as well as seasonality in concentration anomalies. In summer short trajectories often have their origin in air coming from areas in the Arctic and areas with small sources of methane. In contrast winter trajectories are frequently longer bringing air from sources farther away from Ny-Ålesund. These transports can sometimes be seen as enhanced methane concentrations at the station. Peaks in the measurements with durations of up to several days are a reoccurring feature in the record. Notably in air arriving from central Siberia and Russia, there are positive anomalies in springtime when the thawing of the tundra begins and probably releases methane.

Our trajectory pathways for the years 2000-2003 were compared to a previously developed (Eneroth et al., 2003) climatology for the period 1992-2001 and many similarities were found. One notable difference was that 37% of the total trajectories in the new period come from Europe, Russia and Siberia hence there are less frequently trajectories from Scandinavia and Atlantic than in the previously studied period. This longer-term shift could have an effect on the measurements on Zeppelin station, both in methane and in other species since the winds thus are bringing in air with different “average” origin. Such shifts in circulation can be due to natural climate variations or to even longer term climatic shifts that possibly are human induced. Caution must be taken when interpreting concentration records and attempting to derive source and sink distributions. Such shifts are even severer complications when proceeding further into attempting to determine and quantify possible shifts in the source and sink strengths. This could mean that the need for observation points in an observing network that allows continued quantitative monitoring of suspected regional source areas requires a substantially finer mesh than the presently available international greenhouse gas observational network.

4.2 Russia: Regional and local modelling case studies (Partners 1.1 & 2.1, MGO & RCRSA)

Three case/local modelling studies were carried out within the project. i) Estimation of methane fluxes from an industrial area (Saint Petersburg) on the base of large set of measurements (winter seasons of 1999, 2000) and high-resolution 3D regional modelling results and an inverse trajectory technique. ii) Development of natural methane fluxes parameterization and input into 3D regional model for West Siberian wetland region. iii) Modelling estimation of methane fluxes for West Siberian region. A detailed report of model descriptions and all results is available with important conclusions extracted in this report.

MGO regional model was adapted and applied for the Saint Petersburg region to assess local natural and anthropogenic methane sources. The methane concentration data were assimilated in the 3D transport model (with resolution 55-65° N x 20-40°E): 0.5° longitude and 0.25° latitude. Six hourly meteorological data sets (ERA-40) were prepared and used for the model calculations. Mechanisms of methane concentration field formation were analysed.

MGO regional model (resolution 53-73° N x 62-82°E: 1° longitude and 0.5° latitude) was used for description of methane fields in West Siberian region. Some scenarios of methane emissions from main Siberian gas deposits were developed and input into the model and verified on the base of current field measurements made in summer seasons of 2003 and 2004. NCEP 6-hourly meteorological data sets were prepared for the considered. Scenarios of natural (wetland) methane emissions for summer seasons are prepared based on wetland distributions and published empirical parameterizations.

An example of data and modelling result comparisons for the St.-Petersburg area is shown in Figure 4.3 We note that timing of peaks is in general correct but the height of the peaks is not
captured for all peaks by any of the scenarios which is a common result with this type of event modelling investigation.

Figure 4.3: Distribution of methane concentrations near the surface over St.-Petersburg area for April 24, 1999. Scenario A: 130 mg/(m² day), 45 kT / year. Scenario B: 300 mg/(m² day), 100 kT / year. Scenario C: 600 mg/(m² day), 200 kT/year
Figure 4.4: The top panel shows the surface distribution of methane based on model calculations (for April 24, 1999). The bottom panel shows the column inventory.

The distributions of methane concentration near the surface and of column methane content for the same day and time calculated with the 3D regional transport model for St. Petersburg area are presented in the Figure 4.4. In this case there is a strong influx of Atlantic air masses with lower methane concentrations aloft (see Sec. 4.1 and Figure 4.1 for further examples of such influences). This figure demonstrates that despite strong local surface methane sources with strong influence on the surface values it does not influence the total methane column prominently.

On the basis of MGO 3D regional transport model and simple total methane column model with using of 3D global photochemical model calculation results and spectroscopic data about methane content obtained near the St. Petersburg for studied time period estimates of total column methane formation components were obtained and are presented in Table 4.1.

Table 4.1: Model estimation of different atmospheric parameters variation input into atmospheric methane column

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Layer</th>
<th>The range of parameter variability</th>
<th>Change of atm. column methane content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical profile of methane mixing ratio (for surface pressure 1000 hPa)</td>
<td>0-1 km</td>
<td>2.8-1.8 ppm*</td>
<td>~1.8 %</td>
</tr>
<tr>
<td></td>
<td>0-2 km</td>
<td>2.8-1.8 ppm</td>
<td>~3 %</td>
</tr>
<tr>
<td></td>
<td>1-11 km</td>
<td>1.6 ppm - 1.8 ppm</td>
<td>~7 %</td>
</tr>
<tr>
<td>Methane content</td>
<td>Above 11 km</td>
<td>7.1-7.8 \times 10^{-18} \text{ mol cm}^{-2} \text{ (seasonal variability)}</td>
<td>&lt;2 %</td>
</tr>
<tr>
<td>Tropopause height</td>
<td>from 8 km to 12 km</td>
<td></td>
<td>~1.5%</td>
</tr>
<tr>
<td>Surface pressure</td>
<td>0 km – upper boundary of atm.</td>
<td>1000 hPa – 1030 hPa</td>
<td>2.5 %</td>
</tr>
</tbody>
</table>

* Methane concentration decreases linearly from 2.8 ppm (surface layer) to 1.8 ppm (at 1 or 2 km correspondingly) and then it is constant up to 11 km

** According to 3D global photochemical model MEZON.
This result has direct implications for how exact column inventories remote-sensing techniques must reach in order to detect regional and local fluxes. These regional problems thus require accuracies of single percents of total column inventory for the bottom of the troposphere.

Annual methane emissions are estimated as \(~100\) kT from St. Petersburg area and vicinities on the basis of 1999 and 2000 winter measurements.

![Figure 4.5](image-url)

**Figure 4.5:** Distribution of natural methane fluxes using described parameterisation for August 28, 2003 and gas deposits leakage according to official GAZPROM data for 1999. The sites of methane sampling during summer field campaigns of 2003 and 2004 are indicated by asterisks.

To estimate the methane distribution over the West Siberian region, which is one of the strongest methane sources of the world, we must estimate natural methane sources (from vast areas of marshes) as well as anthropogenic methane emissions from gas fields. Figure 4.5 shows the distribution as calculated with available parameterizations. Over the considered area natural methane fluxes vary from 45-50 mg/(m^2*day) (or \(~100\) kT/day) in the beginning and in the middle of August to 8-10 mg/(m^2*day) (or \(~20\) kT/day) at the end of September. This huge methane flux from natural sources depends on temperature and can increase under observed conditions of warming Arctic. These strong variations and implications for sampling strategies and modelling are discussed further in section 5.

Comparison of measured and calculated methane concentrations for 3 sampling sites (Salym, Novy Port and Korotchaev) for 2003 were performed. Figure 4.6 presents one example to illustrate the origins of some important conclusions.
Novy Port (67°41’N, 72°52’E)

Figure 4.6: Comparison of measurements and modelled values during the field campaign 2004.

Scenario 1 – natural methane fluxes combined with gas leakage of ~1.8 Mt CH₄/year

Scenario 2 – natural methane fluxes as a half of Scenario 1 combined with gas leakage of ~1.8 Mt CH₄/year

Gas deposits leakage only corresponds to gas leakage of ~1.8 Mt CH₄/year in the absence of natural methane fluxes.

The concentration data are instantaneous flask samples (stars in Figure 4.6) which leads to a sparse data set which frequently gives inconclusive results regarding the capturing of the sharp peaks predicted by the models. For studies of processes on this (local) scale continuous measurements are necessary. The gradients are steep close to these strong sources which implies a requirement for many stations (or rapidly moving instruments) to capture the emission plumes.

During the 2004 summer sampling campaign a set of measurements was obtained in two points of West Siberian region: Novy Port (67°41’ N, 72°53’ E) and Korotchaevo (65°58’N, 78°07’ E).

In spite of the good agreement between measured methane mixing ratios for the summer 2004 data and calculated ones (in average) many maximums of data are not reconstructed by the model, probably due to not very detailed description of all possible sources of methane located in this region with high density of gas deposits. More work on gathering methane leakage intensity and distribution is needed. The natural flux for Korotchaevo area is estimated as 7-10 mg/(m² day) (as an averaged value for an area of 55.5 km x 43 km) for September.

The parameterisation of natural fluxes used here was originally developed for Northern part of Siberia (Chersky, Tiksi) for low summer temperatures, it should be corrected for warmer temperatures, which were observed during our measurement period, and for temperatures below
0°C, as there are weak natural fluxes even when negative temperatures are observed. Additional chamber measurements in this area can help to develop such methane flux parameterisations in the future which also need to consider the dependency of the hydrological regime.

The set of data obtained in Novy Port in August-September 2003 is inconclusive regarding gas leakage intensity due to either strong influence of natural fluxes in the first part or possible presence of unknown anthropogenic methane sources. The set of data obtained in Korotchaevo in August-September 2003 reveals strong influence of gas leakage deposits but these data are not sufficient to make definite estimates of anthropogenic fluxes intensity. This is due to the fact that the sites location relative to gas deposits does not allow proper separation of the input of different gas fields in this set of data.

For correct estimates of gas leakage from gas deposits it seems necessary to organize continuous methane concentration measurements in Korotchaevo during several months, especially in winter season. The same kind of measurements in Novy Port would be useful as well, taking into account the possible methane leakage from new gas deposits developed in the offshore area of the Ob bay. This again illustrates the need for data with high temporal and spatial resolution for local/smaller region studies. Above it has been concluded that the backbone observational network can give robust results over averaging times extending from days to a few weeks. The ability to resolve intensities of hot spot sources (as the Ob river estuary) requires campaigns close to the emission sources with data of high temporal and spatial resolution.

4.3 Estimate of methane emission in Russia by the inverse method (Partner 1.1, RCRSA)

The atmospheric boundary layer (ABL) budgeting technique was used for methane emission estimate. The technique is based on the treatment of time series of concentration measurements at a point near the surface. The idea of the treatment is the same as in Zinchenko et al. (2002). The new development is the fitting of the effective thickness of nocturnal accumulation layer using as the base HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (see Sec. 4.4). We use vertical diffusion of heat energy from the surface as a tracer to determine the height of the night time accumulation layer. The nocturnal ABL is interpreted as natural collector and integrator of CH4 from ground level sources. In warm seasons the atmospheric boundary layer (ABL) consists of three major parts: a very turbulent convective boundary layer (CBL) (mixing layer in the day-time), a less turbulent residual layer containing former mixing layer, and a nocturnal (stable) boundary layer (NBL).

The developed technique has been applied to estimate the methane emissions in the St. Petersburg region and in wetland regions within the West Siberia Lowland (WSL). The results of the St. Petersburg estimates for 2004 have been compared with those from 1996 and 1998. The difference is not more than the possible error of estimation. The WSL methane fluxes are close to those known from literature fluxes within the Hudson Bay Lowland.

The results of the St. Petersburg estimates for 2004 have been compared with those for 1996 and 1998, recalculated by using more correct meteorological data from HYSPLIT. In the St. Petersburg region, emission rates range from 1.4 to 3.3 g (CH4) km⁻² s⁻¹ without any significant difference between 1996 – 1998 and 2004. The emission value refers to specific air mass transport; the wide range of the emission values is due to the non-uniform distribution of industrial sources in the St. Petersburg region. On the basis of observations at Salym methane emissions have been estimated. The average CH4 flux was about 24 mg (CH4) m⁻² d⁻¹.
4.4 Trajectory studies with the HYSPLIT 4 model (Partner 5, UIG)

In this project much use has been made of the Hybrid Single Particle Lagrangian Integrated Transport model, developed at the Atmospheric Research Laboratories, Maryland. Hysplit 4 is designed to support a wide range of simulations related to the long-range transport, dispersion, and deposition of pollutants. Simulation output results can vary from simple trajectories to more complex air concentration contour patterns. Calculations can be performed on archive or forecast meteorological data, or a combination of both. The current version (Hysplit 4) has substantially updated algorithms for stability and mixing and is capable of handling multiple and nested meteorological data and concentration output grids. The model calculation method is a hybrid between Eulerian and Lagrangian approaches. Advection and diffusion calculations are made in a Lagrangian framework while concentrations are calculated on a fixed grid.

The network of existing stations (see WP 1) was assessed in terms of the mutual or shared back trajectories. This allows one to gauge the degree to which a particular station might contribute to a modelling programme, which tries to estimate emissions in the region. When two (or more) stations share a back trajectory, then measurements from the first station can initialise the model, and represent the air mass conditions prior to sampling at the second station. Any differences between the stations can be ascribed to emissions, sinks and other processes that have occurred as the air travelled between stations.

![Figure 4.7: Composite of daily 12.00 GMT back trajectories for the network, indicating densities of coverage.](image)

Figure 4.7 shows a composite of daily 12.00 GMT back trajectories indicating densities of coverage. Figure 4.8 shows only those segments of trajectories where prior to arrival at the sampling site, the air mass has passed within two degrees of any of the other sites in the network. Sites in Network are: Heidelberg, Kasprowy, Mace Head, Ny-Ålesund, Pallas, Paris, Puy de Dome, RHUL, Schauinsland, St. Petersburg.
Stations on the western fringe of Europe tend to have relatively few shared back trajectories that arrive from other stations. This is due to the prevailing westerly airflows in the North Atlantic region. However, they commonly share back trajectories with other stations further east, thereby the western stations can often act as the background or initialisation, from which to investigate the emissions in regions between stations. This is especially the case as the measurements made at western marine or coastal sampling stations tend to be representative of a larger region, than measurements taken inland.

A visual inspection of the network from this shared trajectory perspective indicates certain gaps in the coverage of the present network. The Mediterranean region and southern Europe are poorly covered. New stations in this region are very desirable. Prospective station sites are chosen on the basis that at least some limited air-sampling programme already exists at these sites. One good criterion is that the site is included on the NOAA CMDL flask-sampling programme. Addition of sites in Portugal, Lampedusa, Italy, Crete and Cyprus were considered. The sites in Portugal and Lampedusa provided greatest benefit / additional coverage to the present overall network, effectively covering Iberia and the south of France. The potential sites in the eastern Mediterranean appear largely independent of the larger network; typically, air masses in this region neither originate nor finish in Western Europe. They thus extend the network very significantly eastwards but do not add to the knowledge of the present regions.

This back trajectory analysis approach does not give an indication of how the network might be used to compile a synoptic view of chemical weather in Europe. Inspection of Figures 4.7 & 4.8 show that the present network does not allow for any robust statistics on regional fluxes changing with time. With the exception of the core heavily populated area in NW Europe many locations are only overpassed by one trajectory during the entire year (Fig. 4.7). For station-to-station trajectories during the entire year the area touched by more than one trajectory is still smaller. Such individual trajectory studies are useful for case studies. When opportunity gives station-to-station trajectories one gets testing occasions for the averaging and integrating studies that were concluded to be advisable for the regional problem in Section 4.1.
4.4 Global Modelling of Atmospheric Methane (associate of Partner 1, Cambridge)

Three-dimensional atmospheric model simulations of methane and its isotopic composition have been used to explore our understanding of the geographical distribution of CH$_4$ emissions on a global scale (see Figure 4.9). Four large-scale problems were found with the simulated methane distribution: (i) the modelled CH$_4$ interhemispheric gradient was 40% larger than that determined from atmospheric observations; (ii) modelled $\delta^{13}$C-CH$_4$ values were lighter than measurements suggest by about 0.3‰; (iii) model northern hemispheric CH$_4$ seasonal cycles show larger seasonal variability than seen in measurements; (iv) there is a phase difference of approximately one month between modelled and observed CH$_4$ seasonal cycles in the remote Southern Hemisphere (see Figure 4.10).

To identify possible causes of these shortcomings in the model, further experiments colouring methane emitted from each prescribed source were performed. The results suggest that differences between observed and modelled methane mixing ratios described above could be significantly reduced by decreasing methane emissions from wetlands and/or fossil fuel sources. Lowering emission from wetlands or anthropogenic (fossil fuel and waste) sources would decrease the modelled CH$_4$ latitudinal gradient, bringing it closer to observations. A solitary reduction in the isotopically heavy fossil fuel source would, however, make the global emission scenario (which is already too light) even lighter. A decrease in the fossil fuel source would therefore need to be accompanied by an increase in another isotopically heavy source (e.g. biomass burning), or a significant decrease in an isotopically light source, such as wetlands. Decreasing emission from these two sources would also likely improve the agreement between observed and modelled methane seasonal cycles in the northern and southern hemispheres.

Figure 4.9: Annual mean modelled surface CH$_4$ using 1998 meteorology.
Figure 4.10: Monthly mean simulated CH$_4$ and $\delta^{13}$C-CH$_4$ (red lines) compared with NOAA/CMDL monthly mean measurements for 1998.
Workpackage 5: Synthesis

5.1 Assessment of problems in Monitoring

The goal of MethMonitEUr has been to develop a sampling strategy for a long-term European network. The present study emphasizes the regional/continental scale (i.e. the European dimension) and has concentrated on formulating a cost effective network on this scale. The sampling strategy that evolves is dependent on this choice of study scale and it also remains model dependent despite the use of a cascade of models with different resolutions. Future societal needs can be at other scales (e.g. local scales) and will require further analysis of the problem with new models and other considerations. A “final” network design will to some extent lock the scientific exploration to problems on specific scales. New methods will continuously appear and whenever new opportunities for spatial and/or temporal coverage emerge vivacious questioning of the network design should automatically ensue. It is therefore of paramount importance for a sustainable network design to contain an integrated research component for continuous network development.

From Figure 4.1 and the discussions we can draw conclusions regarding the needs in a monitoring network. To identify sources from individual episodes (concentration anomaly events) at a station trajectory or transport models are useful tools. A quantitative source determination from the amplitude of such single episodes is, however, not possible due to the uncertainties in the meteorological simulations underway from the source areas, and due to the heterogeneous distribution and strength of the sources. Statistics on changes in amplitude height and frequency of occurrence of such episodes can provide semi-quantitative information provided we have sufficiently long times series of measurements. A long-term observational network should therefore contain a number of stations with high temporal resolution concentration data within the areas of emission, several along the periphery of the active region and a few remote stations.

Continuous isotope measurements are still at the development stage with high costs and reliability problems if placed at a remote monitoring station. It appears that integrating isotope samples to determine regional gradients are a necessary component of a monitoring network whereas continuous measurements will have the same interpretive problems as the single station concentration data.

We can acquire robust average gradients over time from a relatively sparse (e.g. several hundred kilometres between stations) network of stations cleverly placed around the region (Section 4.1). At this level integrating sampling over time for isotopes is a cost effective and useful approach to strengthen the database.

Flask samples (event sampling) collected sporadically (e.g. the NOAA/CMDL network one per week) are not sufficient for rapid determination of gradient shifts. In a system with large variability on time-scales shorter than the sampling frequency there will be a large element of randomness built into the dataset. Integrating sampling techniques have become “unfashionable” but have clear assets in cost effectiveness when taking into account the limits of interpretive capacity the meteorology imposes. The flask sampling programs are, nevertheless, extremely important both for giving global average pictures and most significantly to provide a completely independent verification of the long-term monitoring instruments performance.

Determining fluxes between land and atmosphere from measurements is a complex issue. The vegetation cover is patchy and heterogeneous. The terrestrial pools of carbon and nitrogen have storage times ranging from minutes up to thousands of years. The slow reservoirs (soil carbon) are large and could potentially under climate change liberate large quantities of carbon dioxide and methane. Some storage accumulates over decades to hundreds of years to then be released.
catastrophically (tree growth – forest-fire cycles). Methane and nitrous oxide have complex formation processes that are not only carbon inventory related but also influenced by climatic factors.

The land-atmosphere exchange of material can be studied on both sides of the domain boundary by measuring rates of change in inventory.

Terrestrial inventory studies have some relevance for carbon dioxide. Inventory studies for carbon dioxide are faced with detecting small changes in storage in a large reservoir. The exception being calculating fluxes from a region following a short time-scale drastic change (the aforementioned forest fires, clear-cutting or other land-use changes). The terrestrial inventory measurements thus have difficulties in detecting unperturbed fluxes with great precision. Detecting the rate these uncertain fluxes are changing in response to climate change will contain even larger uncertainties.

Methane and nitrous oxide releases are controlled by processes essentially decoupled from storage. The fluxes of methane are small compared to the total amount of available carbon. Nitrous oxide fluxes are small compared to total nitrogen in the soil but the relation is not as unfavourable as for CO₂ and CH₄. The only prerequisite for methane and nitrous oxide exchange is that there is sufficient carbon available to accommodate respiration processes and climatic conditions need to be favourable. For all three gases we conclude that terrestrial inventory studies are crude tools to determine fluxes and in particular flux rate response to climate change. Moreover, expanding from localised measurements to regionally valid conclusions remains a challenge due to the heterogeneity of the landscape.

On the atmospheric side of the problem we have a somewhat different situation. Here the fluxes can create concentration changes that are easily measured with available instruments. The problem is thus not detecting the rate of change of the burden in the air but rather what volume of air that the burden calculation should be integrated over. Utilizing the atmosphere as an integrator for larger regions therefore requires an understanding of the mixing and transport characteristics. Mid-latitude meteorologists have always utilized nomenclature like “fronts” and “air-masses” when air from one meteorological realm is replaced by another. These shifts are driven by mid-latitude storms. From the scales of these systems and meteorological records we can garner characteristic spatial and temporal scales for which measurements are necessary to be able to characterize the areas which the atmosphere is providing “integrated” air samples over. Meteorological observations are much more plentiful than can realistically be expected of an observational methane network during the coming decade. The meteorological fields can, therefore, be leaned against which can allow adjustable averaging periods and thus a maximization of the extracted methane source/sink information.

Averaging data over periods longer than the synoptic variations appear robust in the model simulations. The atmospheric “integrations” are, however, incomplete and tangled by mixing that needs further consideration in the interpretation. The sources and sinks change in strength continuously through the seasons as well as the prevailing wind patterns which implies that there in principle is no valid averaging time. The attempt to filter out synoptic meteorological variability will also filter source/sink variability and averaging may also mask some of the ongoing seasonal shifts in circulation. In particular we need to understand better how rapidly the methane source function changes on the regional scale (see Section 4.2). There are strong meteorological feedbacks on the natural methane source, which are expected to systematically co-vary with different sections of a synoptic weather system. To resolve this complication in interpretation, continued process studies with regional to local dimensions are needed at least on a campaign basis.

The global background is, furthermore, changing which means that the regional/continental study must be capable of detecting internal change towards a changing background. The global
networks provide basic background information but a European sampling network must nevertheless have some stations on the periphery to constrain the inflow characteristics.

Spanning the scales from local measurements to the global scale requires sophisticated atmospheric models as well as a sufficient number of measurements to constrain the models. Theoretically the perfect global model will only require one measurement for verification but models are far from perfect. We nevertheless have confidence in meteorological forecasts for several days, which indicate that it suffices with fewer measurements than one in every grid-box of the model for constraints. Simulations with present models indicate that we need for a European scale study measurements that can yield continental scale average weekly-monthly means and can then concentrate on determining fluxes necessary to maintain these mean gradients. This does, however, also imply a limitation on the attainable temporal resolution of estimated flux variability since they too will be averaged over the same times.

Vertical measurements are useful but maybe overestimated in significance. The methane sources are on the surface. The mid to upper troposphere has rapid East-West circulation times on mid latitudes (< 2 weeks around the globe) whereas the vertical mixing rate of the mid-latitude troposphere is of order 1 month. Regional and even European scale fluxes will be rapidly erased and difficult to distinguish even as an average over long time in levels above the boundary layer. Sparse sampling at altitude, both in space and time, due to logistical reasons (airplane availability) or in the case of towers, in space, due to difficulties with infrastructure investments and costs of running will limit the availability of vertical profiles.

The utility of satellite measurements remains limited for methane. The large concentration deviations are in the lowest part of the troposphere and the largest changes seen will only constitute a few percent of the total column methane inventory. The satellite instruments must, therefore, be capable of determining total column concentration within at least 1% and probably also with 500 meter resolution in order to compete (or even contribute to) with regional studies based on ground based measurements in a network as suggested here (see Section 4.2). Recent developments show that the SCIAMACHY instrument (Frankenberg et al., 2005) can give some regional information with the required resolution but with limited number of sweeps per day for a single satellite and to date mainly successful in southern Europe and lower latitudes.

Clearly satellite data and vertical profiles are useful where available but the backbone of a methane sampling network must be built on surface monitoring stations unless new breakthroughs in vertical sampling technology or remote sensing techniques occur.

5.2 Design of a new monitoring system

A sustainable cost effective monitoring system to determine regional (European) source estimates of methane must contain several elements.

1) Continuous ground based measurements at locations spread across the region at stations with several other continuous gas measurements in parallel.

2) Isotopic data collected in integrated samples at all locations.

3) An affiliated long-term research and modelling program that utilises and develops the network continuously.

4) A QA/QC mechanism with continued round-robin programs and links to international calibration centres.

5) A parallel independent flask-sampling program to have continuous site quality control mechanisms built into the network.

6) Utilisation of vertical profiles where available.
7) Best use of satellite data in combination with the ground based network backbone.
8) Introduce continuous isotopic measurements when available.
9) A capability to perform case/process studies for hot spot areas to quantify smaller scale source areas.
10) Sustained long-term financing for all these components.

MethMonitEUr has brought many of these points together but some further development is necessary. The number of stations requires some additions in particular in Southern Europe, Russia and in central/southern Scandinavia. Point 2 needs implementation but is clearly desirable to achieve. Points 3 and 4 have been developed and demonstrated within the program but need sustained support to become firmly operational on the long term. Point 5 is in place at some locations but not all. Regarding point 6 there is a clear need and desire to integrate efforts with the CHIOTTO activities and ongoing aircraft activities. Point 7 is clearly a future activity that will develop and MethMonitEUr seeks integration with these opportunities as the methods approach the level of information that the regional methane problem requires. Point 8 is an ongoing activity whose implementation is imminent. Point 9 capabilities are demonstrated in Section 4.2 and in the discussions regarding Figure 1.22 even if the design of case study experiments is still under development. Clearly there is a need for a European long-term methane monitoring consortium as implied by point 10.

Site Selection

A cost effective and pragmatic approach is of course to make best use of the existing network of stations. Both, with regard to the economic investments already made but in particular regarding the heritage of the time-series already accrued. The network is, however, dense in central (Western Europe) and sparser elsewhere. Southern Europe and particularly the Mediterranean area is only sparsely sampled. The Iberian Peninsula is somewhat meteorologically independent of the rest of Europe and thus poorly covered by the present network. Two stations are probably necessary to constrain the influences from the Peninsula. Towards the Eastern Mediterranean there is a need for stations to monitor the inflow from the possible large fluxes from gas fields in the Near East. Scandinavia is a large European area that should be complemented with at least one continuous station. Finally there is a clear need to complement with stations in Eastern Europe and particularly in Russia. On the European side of the Urals a North-South concentration distribution is required with at least three stations in Russia. Extending the problem further east increases the number required further. These locations must be co-sited with other gas and meteorological measurements. The exact locations within the realms mentioned remain to be discussed but the gaps need to be filled during the coming years to implement a full European coverage of regional methane monitoring at a level that allows quantitative assessment of European sources.

5.3 Synthesis of understanding of European methane emissions and the use of Monitoring for verification of greenhouse gas measurements and estimates

Synthesis workshops were held. The workshops brought together both measuring expertise and also modelling requirements. The workshops also co-ordinated links with Carbo-Europe, especially where they concern methane Meth-MonitEUr was based on an ad hoc gathering together of available efforts, to create a better whole. The budget was necessarily extremely
limited. The workshops considered the design of a better future methane monitoring system for implementation in the 6th EAP. The workshop also discussed the creation and management procedure of a database of methane monitoring records from the European programme, in a form that can be used together with other international data sets.

5.4 Assessment of needs for long-term programme

Methane is very important as a greenhouse gas. Hanson and Sato (2001) showed that its total contribution to global warming to date, including indirect effects, was perhaps half that of carbon dioxide. Recently, Shindell et al calculated and emissions-based assessment of the role of methane and showed that its warming impact to date may be as high as 60% of carbon dioxide to date.

Methane is badly neglected by Europe, and the main burden of global monitoring falls on the USA. The needs are thus very obvious – Europe must contribute.

In detail, two types of need are identified:

a) the need for much better scientific understanding of the methane problem.

b) the need for long term support for basic monitoring.

These two needs are best addressed within the present European Frameworks by

a) a STREP project, focussed on methane science as well as on N₂O. This would best be a single STREP, focussing on basic science. The addition of N₂O is wise as it maximises the synergy between the study of these two Kyoto gases.

b) a supporting commitment to monitoring and intercomparison of national programmes as part of a long-term contribution to regional and global monitoring. Part of the monitoring work could be subsumed within the STREP, but there is also a need for underlying low level long term support for measurement.

5.5. Technical proposal for an EU Methane and N₂O Monitoring and Modelling programme

The Meth-MonitEUr group together with partners from Chiotto and other partners, has shaped a new proposal for European methane monitoring. The final text of this proposal is necessarily delayed as the final text of the next Call is delayed, but Table 5.1 outlines the structure of the proposal and the regional division of task leadership.
### Table 5.1. Methane and Nitrous Oxide Monitoring in Europe

**Type of instrument:** STREP  
**Duration of the project:** 3 Years  
**Likely partners:** GB, D, F, N, Ru, PL, FIN, EU, NL, HU, CH and subcontractors

#### Workpackage list (full duration of project)

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<td>36</td>
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**References:**


Section 6.4 Conclusions including socio-economic relevance, strategic aspects and policy implications

Meth-MonitEUr has created a basic network to collect inter-compared methane concentration and isotopic time series. The network links to the work of CarboEurope and focusses on modelling methane emissions at regional level (NW Eurasia), exploiting meteorological and ECMWF data.

The Meth-MonitEUr programme has provided improved understanding of methane emissions in Europe; it has added a European contribution to the global effort coordinated by the UN World Meteorological Organisation / International Atomic Energy Agency’s Global Atmosphere watch; it has helped design ways of verifying compliance with Kyoto obligations; and it has provided the basis the design for a better, more comprehensive European methane monitoring programme.

Socio-Economic relevance

The main socio-economic relevance is the insight into greenhouse gas reduction: that Europe has significant methane emissions and hence cutting methane emissions is a viable way to reduce the global warming impact of the European economy.

Methane is not simply a greenhouse gas – it is central to the European economy. This project, by identifying the scale of methane leakage, has shown the extent of economic loss from waste.

Meth-MonitEUr has also improved mobility and interaction between methane scientists in Europe. By linking so many of the main laboratories as a coherent group, it will greatly improve the contacts between the labs, and will pool their shared knowledge.

Strategic aspects

How can Europe most efficiently cut its greenhouse gas impact? – one powerful route is via methane. The long-term future of the European Union will be strongly influenced by global climate change, not only as it affects Europe but from the spin-offs in famine and suffering from climate change as it affects other parts of the world. The knowledge of methane in Europe: where it is emitted, how much is emitted, and how to reduce it, is crucial to addressing this challenge.

The Russian dimension of the project is also of major strategic value. Russian gas is one of the largest sources of energy for the European Union. Russian gas leaks are very important on a global scale as are natural emissions from Russian wetlands. These emissions need wide observation over large parts of the Northern Hemisphere (i.e. Pallas, Ny Ålesund, Alert), as well as field campaigns in source areas. Human-induced emissions from gas systems and wetland emissions (summer) have been assessed by field measurements in the source regions and remote monitoring in Europe, the Arctic, Eastern Russia and Siberia, and the have been modelled.

Policy implications

The winds carry no passports – the national scale is too small for understanding European emission. Europe needs to address Kyoto issues on a pan-European basis. Methane is the anthropogenic greenhouse gas second in importance after carbon dioxide. In terms of actual warming impact at the present day, methane has approximately half or more of the impact of carbon dioxide (e.g. see Hansen and Sato, 2001, Shindell et al. 2005). Moreover, methane levels can quickly be reduced, within a few decades, relatively cheaply compared to carbon dioxide.

Verifiability is essential if Kyoto is to succeed (Nisbet 2005). This project has shown that it possible to verify European methane emissions by careful atmospheric monitoring and modelling, to test national and community-wide emission inventories.
The Meth-MonitEUr network is very basic, and represents all that can be accomplished given the very small budget that is realistically available, but provides a basis for a proper European response to the need for methane monitoring, and serves as a pilot for future work. When effective, the network will provide the dataflow for the independent verification of methane emissions that is needed if Europe is to meet the needs of the Kyoto process.


Section 6.5. Dissemination and exploitation of the results

The chief dissemination is via scientific papers and presentations at meetings. A list of papers to date in the 24 month term of the project is appended: note that the majority of papers will follow the project as there is typically a 1-2 year writing, submission and review process before a paper is published.

The focus of the project is monitoring. The database created by the project is a core part of the long-term dissemination strategy. This database will be made available to qualified modellers and will be an essential resource to all those assessing the European methane budget from the top down.

Main literature produced
(partner order)

Presentations
Pedersen, Ine-Therese "Investigation of how observed methane concentrations in Ny-Ålesund are influenced by atmospheric flow patterns". Third International Symposium on the Arctic Research and Seventh Ny-Ålesund Scientific Seminar, Tokyo, Feb. 22-24, 2005. (Oral presentation)


Eneroth, Kristina Tuula Aalto, Juha Hatakka, Kim Holmén, Tuomas Laurila and Yrjö Viisanen “Atmospheric transport of carbon dioxide to a baseline monitoring station in northern Finland”, Tellus, in press.


Pedersen, Ine-Therese and Kim Holmén "Investigation of how observed methane concentrations in Ny-Ålesund are influenced by atmospheric flow patterns". Submitted.


Conference presentations:


